



National Institute for Public Health
and the Environment
Ministry of Health, Welfare and Sport

Quality of the *Gradko* passive samplers in the MAN monitoring network





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Synopsis

Quality of Gradko's passive samplers in the MAN monitoring network

The Ammonia Measurement Network in Nature Reserves (MAN) measures ammonia concentrations in the air at approximately 280 locations in nature areas as part of the Integrated Approach to Nitrogen (PAS). The concentrations are measured using Gradko passive samplers that are exchanged every month. These samplers have a number of important advantages: their compactness, inconspicuousness and simple exchange. In addition, they are also cheaper than other commercially available samplers. A disadvantage, however, is that Gradko samplers are less accurate than other more expensive passive samplers. To overcome this disadvantage, the Gradko samplers in the MAN are calibrated every month to six reference instruments from the National Air Quality Monitoring Network located across the Netherlands in regions with varying pollution levels.

In this report, the quality of the Gradko passive samplers is investigated before and after the performed calibration. Without calibration, the measurements of the Gradko samplers are systematically too high, especially in the low concentration range. After calibration, this systematic difference is eliminated. The calibration procedure also corrects the observations for meteorological influences, which reduces noise in the measurements. The accuracy of the calibrated Gradko measurements is very similar to the accuracy of various other low-cost measurement techniques.

Because the measurement locations are in public areas and the MAN makes use of the efforts of volunteers and site managers, the simple and robust design of the Gradko samplers is perfectly suited for application in Dutch nature reserves.

Keywords: ammonia, NH₃, nature, Natura-2000, MAN, LML, measurements, measurement network, sampler, Programmatic Approach Nitrogen, PAS

Publiekssamenvatting

Kwaliteit van Gradko passieve samplers in het MAN-meetnet

Het Meetnet Ammoniak in Natuurgebieden (MAN) meet ammoniakconcentraties in de lucht op ongeveer 280 locaties in natuurgebieden, als onderdeel van het Programma Aanpak Stikstof (PAS). De metingen worden uitgevoerd met passieve samplers van Gradko die elke maand verwisseld worden. Belangrijke voordelen van deze samplers zijn hun compactheid, onopvallendheid en de eenvoudige wijze van bemonsteren. Ook zijn zij goedkoper dan andere commercieel verkrijgbare samplers. Een nadeel is echter dat zij minder nauwkeurig zijn dan andere, duurdere samplers. Om dit nadeel te verhelpen, worden de Gradko-samplers elke maand gekalibreerd aan zes referentie-instrumenten van het Landelijk Meetnet Luchtkwaliteit die verspreid over Nederland staan opgesteld in gebieden met verschillende verontreinigingsniveaus.

In dit rapport wordt de kwaliteit van Gradko passieve samplers onderzocht, voor en na de uitgevoerde kalibratie. Zonder kalibratie zijn de metingen van de Gradko-samplers systematisch te hoog, vooral in het lage concentratiebereik. Na kalibratie is deze systematische afwijking niet meer aanwezig. De kalibratieprocedure corrigeert de metingen ook voor meteorologische invloeden, wat de ruis in de metingen vermindert. De nauwkeurigheid van de gekalibreerde Gradko-metingen is dan goed vergelijkbaar met die van verschillende andere goedkope meettechnieken.

Omdat de meetlocaties in publiek toegankelijke terreinen zijn geplaatst en het MAN gebruik maakt van de inzet van vrijwilligers en natuurbeheerders, is het eenvoudige en robuuste ontwerp van de Gradko-samplers zeer geschikt voor de toepassing in Nederlandse natuurgebieden.

Kernwoorden: ammoniak, NH₃, natuur, Natura-2000, MAN, LML, metingen, meetnet, sampler, Programma Aanpak Stikstof, PAS

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Summary

The Ammonia Measurement Network in Nature Reserves (MAN) measures ammonia concentrations in the air at approximately 280 locations in nature reserves, as part of the Integrated Approach to Nitrogen (Programma Aanpak Stikstof, PAS). Most of these nature reserves are Natura 2000 sites that are vulnerable to nitrogen deposition and therefore to ammonia. The measurements are carried out using Gradko passive samplers that are exchanged every month by volunteers and site managers.

There are several reasons why Gradko samplers are used in the MAN. Their advantages are simplicity, compactness, and low cost. A disadvantage is their somewhat lower accuracy in respect to alternative methods. To overcome this disadvantage, the Gradko samplers in the MAN network are calibrated every month to six reference instruments from the National Air Quality Monitoring Network located across the Netherlands. Because the measurement locations are in public areas and the MAN makes use of the efforts of volunteers and nature managers, the simple and robust design of the Gradko samplers is perfectly suited for the application in Dutch nature reserves.

This report presents a study of the accuracy of the Gradko samplers before and after calibration, compared with alternative methods. This study is part of the action plan in response to the recommendations of the international review concerning the scientific quality of the calculation of ammonia emissions and depositions in the Netherlands (Sutton et al., 2015).

Without calibration, the measurements made by the Gradko samplers are systematically too high, especially at low concentrations. The ALPHA-sampler, which has been tested as an alternative, performs better at low concentrations, but apparently suffers from saturation at higher concentrations.

After calibration, however, the Gradko samplers no longer deviate systematically from the reference instrument. The noise in the measurements is then also reduced. This is caused, amongst others, by the calibration correcting the meteorological influences on the Gradko measurements. A comparison with various alternative measurement techniques shows that the calibrated Gradko measurements correspond well with regards to accuracy with state-of-the-art methods such as the ALPHA sampler, DELTA denuder and COTAG. A disadvantage of the Gradko sampler is that it still gives a bit more noise after calibration than, for example, the ALPHA sampler, but this shortcoming disappears after averaging several measured values, i.e. averaging the results of a number of samplers in an area or averaging in time. As a result, this measurement-technical noise no longer plays an important role in annual average values used for model calibration and trend determination.

Because the MAN makes use of the efforts of volunteers and site managers, a simple and robust design of the exchange is of great importance. The Gradko samplers satisfy this requirement. The ALPHA samplers were tested as an alternative at 16 locations for more than a year. Half of the measurements were lost due to problems during the monthly exchange. In comparison, with the Gradko samplers, only 1 in 20 measurements were lost. Other alternatives are also expected to be too complex to allow the monthly exchange by volunteers and site managers to be successful.

Another important benefit of the Gradko samplers is their small size. This not only simplifies the shipping procedure, which is important for the volunteer, but also makes the sampler much less visible in the field than the alternatives. Vandalism only plays a modest role with the Gradko samplers in the MAN, but with a different more eye-catching measurement technique, data failure due to vandalism would likely increase.

This study shows that the Gradko samplers perform slightly less accurately than some of the alternatives. After calibration to a reference instrument, however, the Gradko sampler performs almost identically in this respect, and sometimes even better than state-of-the-art alternatives. With regard to other aspects, especially their inconspicuousness and simplicity of exchange, the Gradko samplers are the preferred measurement instrument.

Introduction

The Ammonia Measurement Network in Nature Areas (MAN) includes approximately 280 locations where the ammonia concentration in the air is measured using passive samplers made by Gradko (Gradko, 2015). The Gradko samplers are based on a design from the 1980s and have a slow sampling rate compared to more novel designs. In comparison, the FERM samplers (used in Sweden), and ALPHA samplers (used in the UK), sample 12 to 20 times faster. They also include a design to reduce contamination and other external influences. The quality of the Gradko samplers is inferior to these techniques. In the conclusions of the review commission on the scientific underpinning of the calculation of ammonia emission and deposition in the Netherlands, it was therefore concluded that the Gradko samplers are not state-of-the-art and therefore cannot be used to reliably assess seasonal patterns, with the exception of high concentration sites.

In this study we show how the Gradko samplers are used and how their quality is improved by calibration to reference measurements of ammonia in the National Air Quality Network. As a result, the calibrated Gradko samplers perform equally to other state-of-the-art alternatives and are thus suited for use in the MAN-network (Chapter 1). We also compare their use with other measurement techniques (Chapter 2) and report on the impact of meteorology and usage in the field (Chapters 3 and 4).

1 Comparison with AMOR measurements at LML locations

In this chapter, we report on the performance of the Gradko samplers compared with the AMOR measurements at those locations where simultaneous measurements are available. These are the 6 locations of the National Air Quality Monitoring Network (LML) where Gradko triplicate measurements are executed to calibrate them monthly to the AMOR measurements. No comparison is made with the DOAS measurements that have been operational since the beginning of 2016 - the new reference to which Gradko samplers are now calibrated - unless stated otherwise in the text.

The AMOR data used include measurements from the locations 131-Vredepeel, 444-De Zilk, 538-Wieringerwerf, 633-Zegveld, 738-Wekerom and 929-Valthermond covering the entire MAN period from 28 February 2005 to 28 January 2015, with the exception of 538-Wieringerwerf, where Gradko measurements were only carried out from 28 December 2008 onwards.

For each location, the triplicate mean of the calibrated Gradko measurements is plotted against the AMOR measurement value. The calibration was performed in two ways:

1. a calibration with application of all LML locations ("corr") as this is default in the MAN, and
2. a calibration where one LML location is not included, namely that location for which the calibrated Gradko values are compared with the AMOR ("corr-1").

For the results per location, see Appendix 1 where the aggregated results for all locations are presented.

Figure 1 shows that the uncalibrated Gradko values are, on average, somewhat higher than the AMOR data from the LML, especially at lower concentrations. The offset of the Gradko measurements, the cut-off of the Y-axis, is approximately 1.5 to 2 $\mu\text{g}/\text{m}^3$ (Appendix 2). This overestimation at lower concentrations by Gradko samplers was already known (Aherne 2011). After calibration, the average deviation is much smaller, 0.20 - 0.25 $\mu\text{g}/\text{m}^3$ for the "corr-1" method, and about 0.20 $\mu\text{g}/\text{m}^3$ for the normal "corr" calibration.

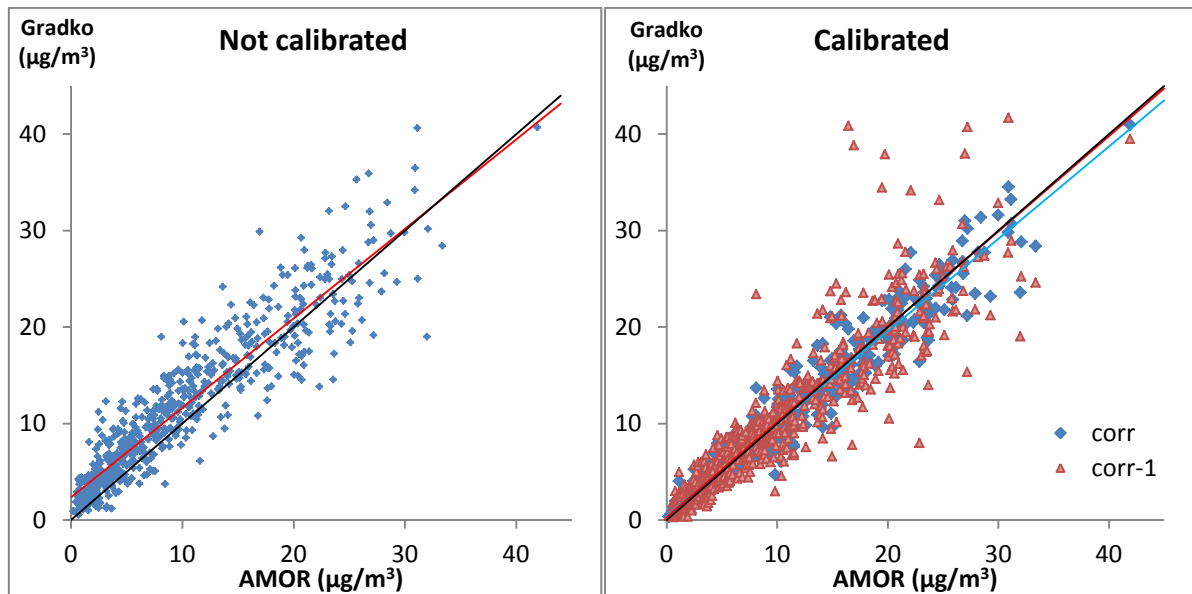


Figure 1: uncalibrated and calibrated Gradko triplicate averages against AMOR measurements from the LML. The calibration of the Gradko samplers is based on all LML locations ("corr") or on all LML locations except the location where the respective Gradko sampler hung ("corr-1"). The black line indicates the 1: 1 line and the coloured lines the linear regression lines.

The spread in the measured values is also smaller after calibration. Only above $15 \mu\text{g}/\text{m}^3$ does the spread by calibration increase with the method "corr-1", because then the measurement location with the highest values (131-Vredepeel) is omitted and the values are, in this case, often calibrated via extrapolation instead of interpolation.

Of all MAN measurements, however, 94% are lower than $10 \mu\text{g}/\text{m}^3$ (average of $4.5 \mu\text{g}/\text{m}^3$) so that the higher part of the measurement series is not really relevant for this study. In the most relevant range for the MAN ($0\text{-}10 \mu\text{g}/\text{m}^3$), the noise in the normally calibrated Gradko values is smaller than that of the "corr-1" method (Figure 2). On average, however, both methods give almost exactly the same result, their regression lines being almost identical. Appendix 2 provides more details on the performance of both calibration methods.

The calibration method according to the regular practice ("corr") has the disadvantage that for tests, measurements are taken which have already been used for the calibration. This method therefore shows a quality of the calibrated Gradko samplers that is too positive. It therefore provides an upper limit to the bandwidth in which the actual quality will lie.

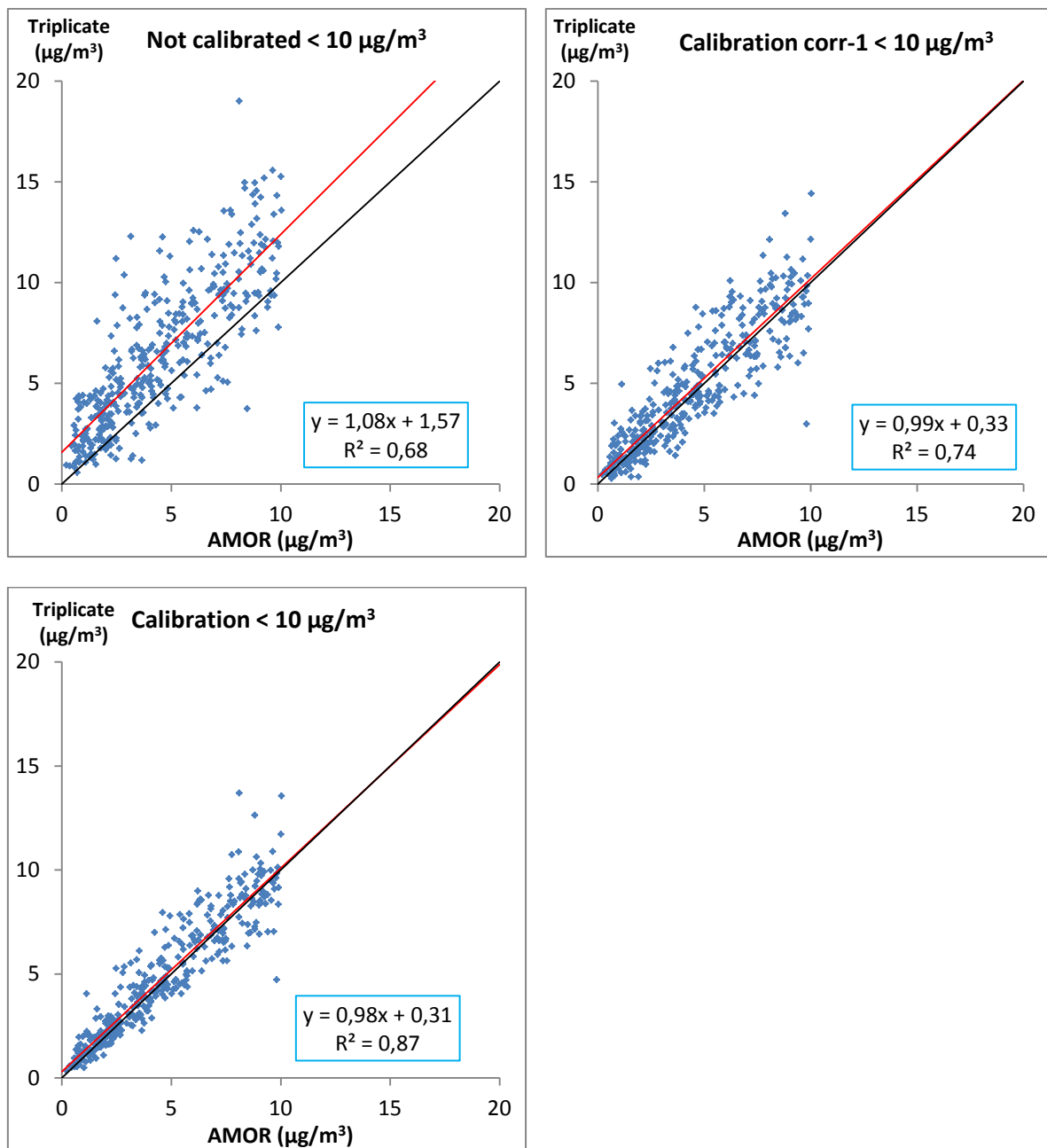


Figure 2: Gradko triplicate averages against AMOR measurements up to 10 µg/m³ from the LML. Calibration of the Gradko samplers is based on all LML locations or on all LML locations without the location where the respective Gradko sampler hung ("corr-1").

The alternative calibration method "corr-1" has the advantage that the calibrated Gradko measurements are completely independent of the AMOR data with which they are compared, so that the comparison at this point is pure. A disadvantage of this method, however, is that the calibration then takes place on the basis of only 5 (and in the years prior to 2009, 4) AMOR locations. Because the usual calibration includes one measuring point more, the calibrated Gradko measurements according to method 2 have a lower quality when compared to the regular method. This is especially the case if the location with the lowest (De

Zilk) or the highest (Vredepeel) concentrations from the series is omitted. This variant therefore gives a lower limit to the bandwidth of the actual quality of the Gradko samplers.

The differences between the two calibration methods are small compared to the difference with the performance of uncalibrated Gradko samplers. Within the MAN range of 0-10 $\mu\text{g}/\text{m}^3$, the systematic deviation between uncalibrated Gradko data and AMOR is about 1.5 to 2 $\mu\text{g}/\text{m}^3$. Both calibration methods reduce this systematic deviation to approximately 0.3 $\mu\text{g}/\text{m}^3$ (Appendix 2). On average, a small overestimation by the calibrated Gradko data remains, but this difference is negligible at higher concentrations compared to the measuring accuracy.

At low concentrations, a systematic deviation counts more, and there this deviation can also be different from the average deviation over the whole series. Determining this deviation in the low range is especially important for the unique Dutch coastal nature reserves, valuable from an international perspective, where the calibrated measured values are the lowest in the Netherlands with an average around 2 $\mu\text{g}/\text{m}^3$.

The offset explicitly indicates whether there is systematic under- or overestimation at low concentrations in the calibrated Gradko data. This axis-section says more about the actual deviation at low concentrations if this is determined on the basis of low measured values. This is because higher measured values also influence the regression from which the offset is determined, whereas they do not say anything about the real deviation at low concentrations. If, however, only very low concentrations are included, the regression becomes more inaccurate and thus does that of the determination of the axial cut. The optimum seems to be, using all data, approximately between 0-5 $\mu\text{g}/\text{m}^3$.

For uncalibrated data below 5 $\mu\text{g}/\text{m}^3$, the offset is 1.3 $\mu\text{g}/\text{m}^3$ (Appendix 2). On this basis, the observations along the coast would therefore be more than 3 $\mu\text{g}/\text{m}^3$. For the calibrated data between 0 to 5 $\mu\text{g}/\text{m}^3$, the offset is lower; 0.16 $\mu\text{g}/\text{m}^3$ ("corr") to 0.25 $\mu\text{g}/\text{m}^3$ ("corr-1") (Figure 3). The calibrated Gradko observations would thus overestimate the low observations of approximately 2 $\mu\text{g}/\text{m}^3$ on the coast by approximately 0.2 $\mu\text{g}/\text{m}^3$. This is only a small systematic overestimation when compared to the measurement accuracy.

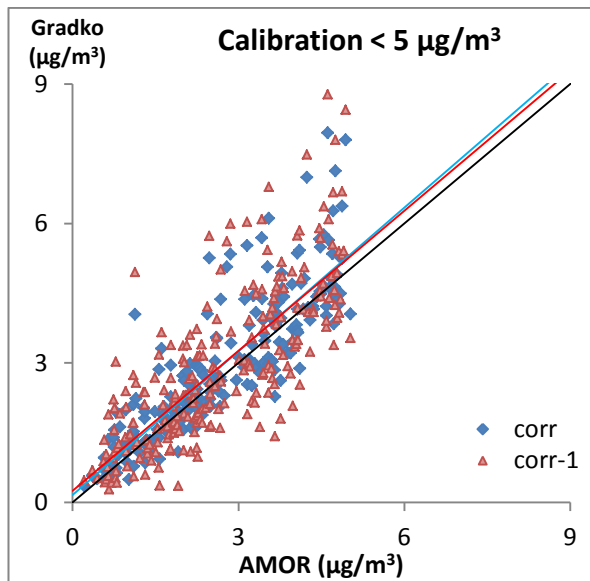


Figure 3: Gradko triplicate averages against AMOR measurements up to $5 \mu\text{g}/\text{m}^3$ from the LML. The calibration of the Gradko samplers is based on all LML locations ("corr") or on all LML locations without the location where the respective Gradko sampler hung ("corr-1").

In addition, there are measurements that directly give an accurate indication of the accuracy at low concentrations, without any comparison with AMOR data. Over the entire series of measurements, an exchanger unintentionally did not remove the black plug caps 62 times when attaching them on the site. This often involved a substitute exchanger in holiday periods, or the first measurements during the training period of the exchanger concerned. If the caps are perfectly closed and the Gradko measurements including calibration are also perfect, the measured value should be exactly 0 in those situations. The measured value over these 62 measurements is, on average, $0.06 \mu\text{g}/\text{m}^3 \pm 0.06 \mu\text{g}/\text{m}^3$. This is even a few times smaller than the systematic overestimation determined before as $0.2 \mu\text{g}/\text{m}^3$ at $0 \mu\text{g}/\text{m}^3$. It confirms that the calibrated observations at low concentrations show virtually no systematic deviation from the AMOR measurements.

2 Comparison with other measurement methods

This chapter describes how the Gradko samplers perform when compared to other measurement methods. Uncalibrated Gradko samplers have already been compared in detail with ALPHA samplers (Tang et al., 2001). An earlier comparison study between ALPHA and calibrated Gradko samplers is available (Lolkema et al. 2015), but it only covers half of the data recorded here. In addition, comparison measurements are available on a more limited scale with DELTA denuders, with COTAG measurements, and with measurements by TNO with samplers that are comparable to the Gradko-samplers.

2.1 Comparison with ALPHA samplers at LML locations and in three coastal areas

The ALPHA samplers were in use in the period October 2011 to December 2012 at 12 locations on the Bosplaat in Terschelling, the Zwanenwater and in Meijendel; measurements taken from 1 sampler per location per month.

In addition, ALPHA-triplicates were used at 4 LML locations: from October 2010 to October 2012 at 444-De Zilk and 633-Zegveld; from October 2010 to August 2011 at 738-Wekerom; and from November 2011 to November 2012 at 538-Wieringerwerf.

2.1.1 Comparison with ALPHA samplers at LML locations

To quantify the reproducibility of the samplers, the ALPHA measurements for each location were plotted against the triplicate mean of the ALPHA measurements and the calibrated Gradko measurements against the calibrated Gradko triplicate average (Figure 4). The normal procedure was used for calibration and validation of the Gradko samplers ("corr"). The Gradko samplers show more noise than the ALPHA samplers, but the variance of the Gradko (0.986) is near to the very good value of the ALPHAs (0.999). This also applies in the low concentration range of 0-3 $\mu\text{g}/\text{m}^3$, where the deviation is small in absolute terms, but relatively higher for both the ALPHA and Gradko samplers when compared to their triplicate averages (Figure 5). The same graphs are used to present each measurement location in Appendix 3.

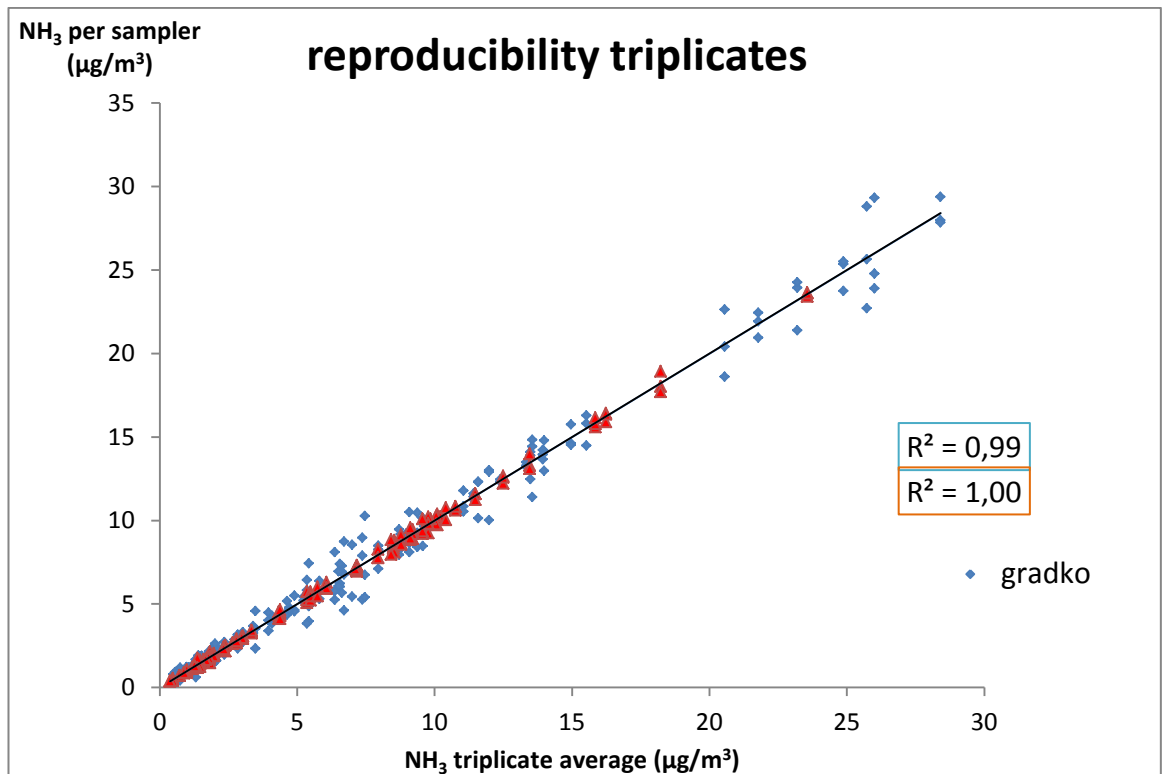


Figure 4: The individual measurements of the ALPHA samplers and the Gradko samplers, plotted against their triplicate average.

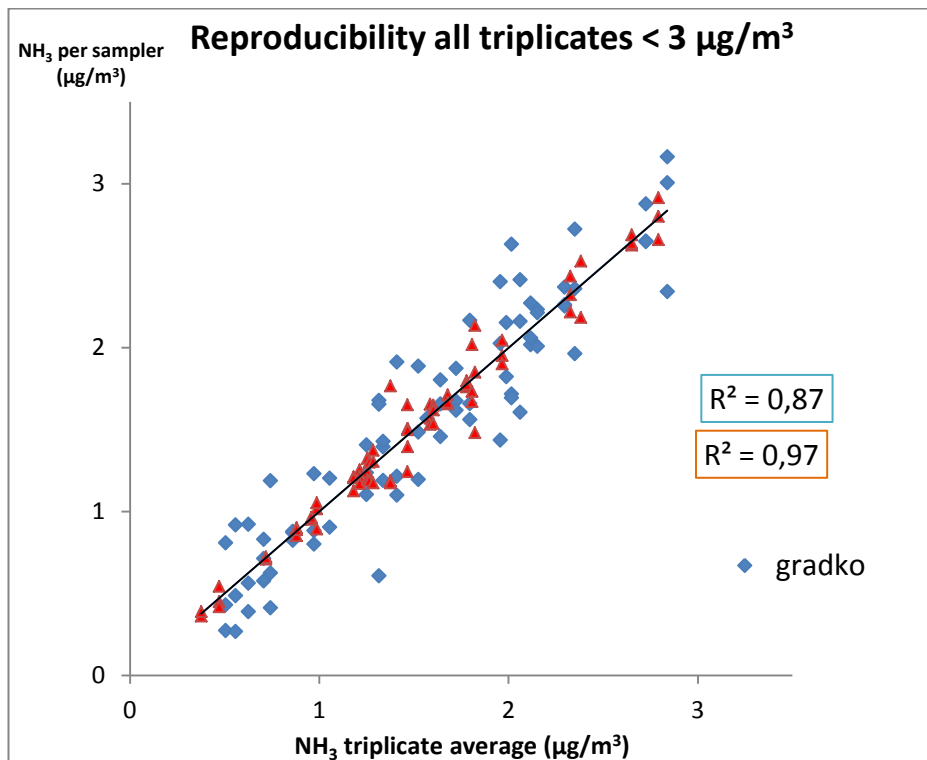


Figure 5: The individual measurements of the ALPHA samplers and the Gradko samplers, plotted against their triplicate average in the range of 0-3 µg/m³.

With respect to the AMOR data, the calibrated Gradko samplers also show more noise than the ALPHA samplers, but both samplers correspond well to the AMOR data up to approximately $12 \mu\text{g}/\text{m}^3$ (Figure 6). Above that, the ALPHA samplers show an increasing deviation downwards; the samplers are probably saturated at higher concentrations and absorb little extra ammonia. The calibrated Gradko samplers show little systematic deviation over the entire measurement range. In the range of $0\text{--}10 \mu\text{g}/\text{m}^3$ relevant to the MAN, the ALPHA samplers perform slightly better in terms of noise than Gradko, but for both samplers there is virtually no systematic deviation with the AMOR data (Figure 7). They score equally well; on both the slope of the regression line is about 1.0 and the offset is approximately $0.1 \mu\text{g}/\text{m}^3$ (Appendix 4).

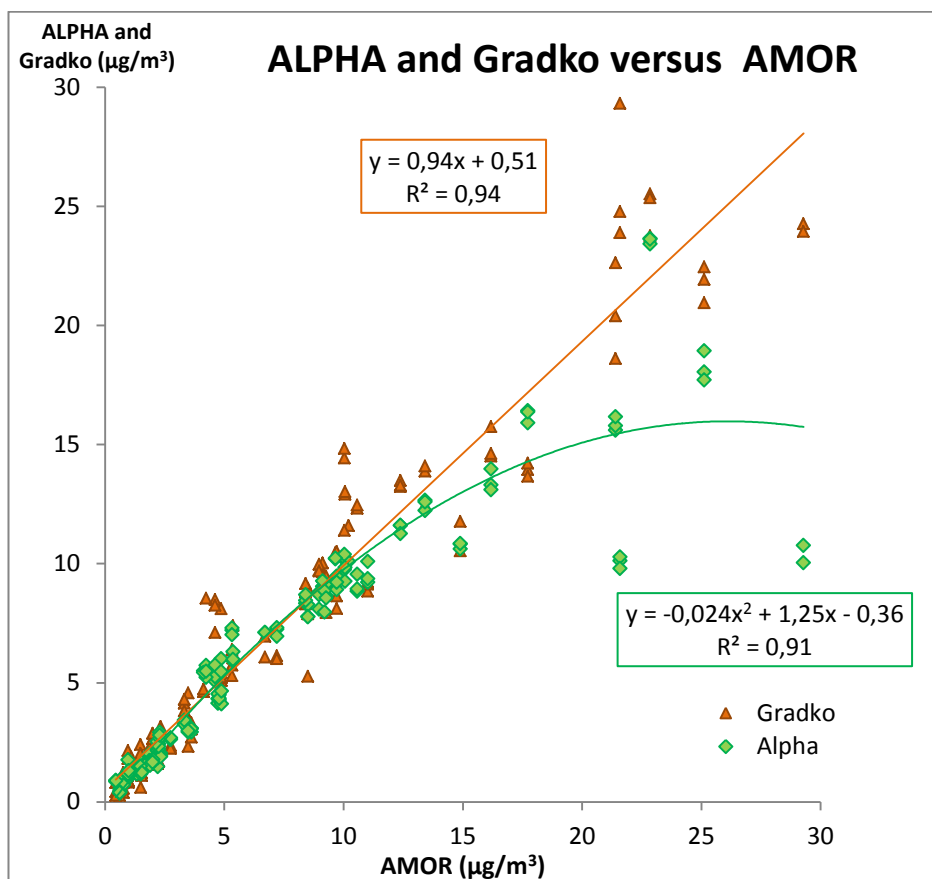


Figure 6: The individual measurements of the ALPHA samplers and the Gradko samplers, compared with the AMOR measurements.

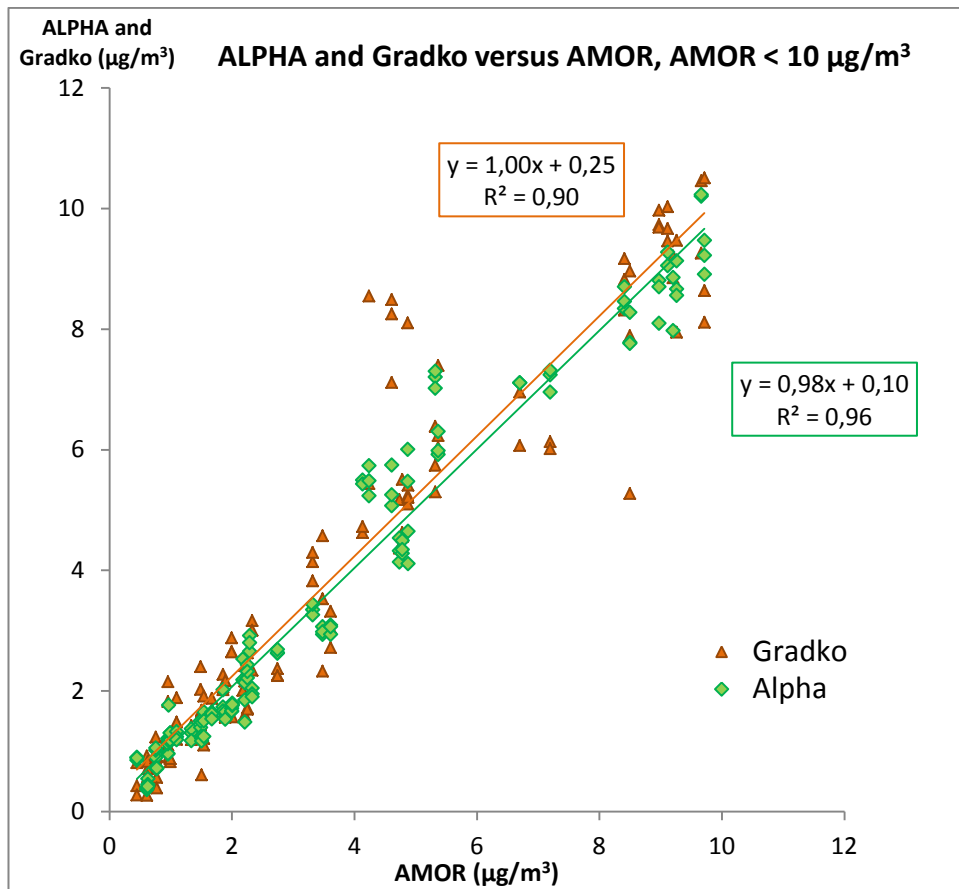


Figure 7: The individual measurements of the ALPHA samplers and the Gradko samplers, compared with the AMOR measurements up to 10 µg/m³.

2.1.1.2

Comparison with ALPHA samplers in three coastal areas

The comparison of the calibrated Gradko samplers with ALPHA samplers at the LML locations is also influenced by the fact that the data from those same locations are used for the calibration (see chapter 1). In addition, it is conceivable that the measurements in the MAN nature reserves may be influenced by other factors than those at the LML locations. Examples of this are the actions of the exchanger and the RIVM transport to the nature reserve and back. Measurements are available that provide both information and, at the same time, are independent of the calibration at the LML locations. These are the simultaneous measurements of ALPHA and Gradko samplers at 12 locations along the coast in the nature reserves: Meyendel, Zwanenwater and Bosplaat on Terschelling. These measurements took place between October 2011 - December 2012.

The main difference between the measurements with both types of samplers in these areas is the high dropout rate among the ALPHA measurements. Chapter 4.2 provides further details on this failure.

The measurements themselves show more noise in the nature reserves than at the LML locations (Figure 8). There are some high Gradko values compared to the ALPHAs, from 4 to 6 µg/m³. These are measurements taken between March and August 2012 at Zwanenwater. In March, the

values of all three ALPHAs in Zwanenwater were low compared to what was observed elsewhere on the coast by AMOR, ALPHA and Gradko. In August, two of the three Gradkos in Zwanenwater were high compared to what was observed elsewhere along the coast. These five "outliers" appear to have been caused by both abnormal ALPHA and Gradko observations. Without these five deviating measurements, the axis cut of the regression line of the coastal nature is only $+0.1 \mu\text{g}/\text{m}^3$ instead of the $-0.25 \mu\text{g}/\text{m}^3$ visible in Figure 8.

The differences between the measured values of ALPHAs and Gradkos are not significantly different in the coastal reserves compared with the LML locations; the two regression lines are close together. Apart from a few outliers, the noise in both series is not substantially different, also considering the specified outliers in Zwanenwater and the relatively small number of measurements. This makes it clear that, after calibration, the Gradko samplers also provide reliable measurements at the low ammonia concentrations in the coastal region without systematic over- or underestimation of the measured value.

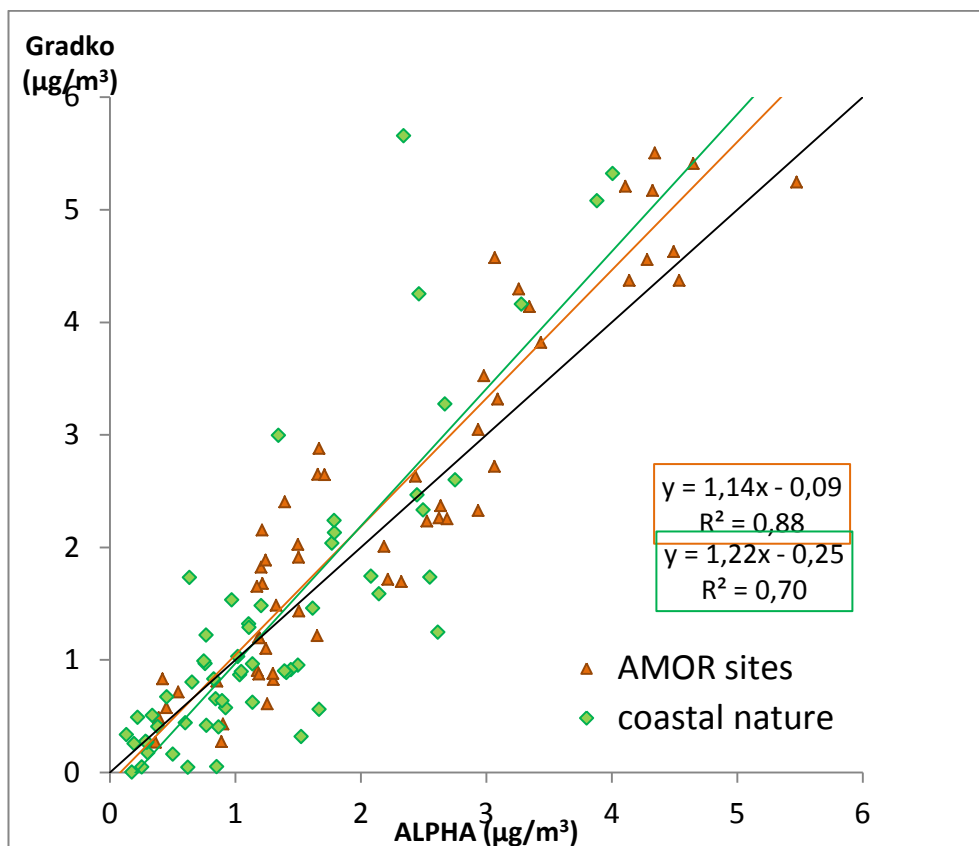


Figure 8: Gradko measurements against ALPHA measurements in the coastal nature of Meyendel, Zwanenwater and Terschelling from October 2011 to December 2012, compared with simultaneous Gradko and ALPHA measurements at LML locations at AMOR values between $0\text{-}5 \mu\text{g}/\text{m}^3$.

2.2 Comparison with AMOR, ALPHA samplers and DELTA denuders on location Zegveld

At AMOR location 633-Zegveld, the ammonia concentration was also measured with a DELTA denuder in September 2003, in collaboration with the Center for Ecology and Hydrology (CEH) in Scotland. In addition, at Zegveld, measurements with ALPHA samplers were carried out from September 2012 to December 2014 as part of the ALPHA measurements at four LML locations and at 12 locations in nature reserves (see section 2.1). The comparisons between AMOR, Gradko and the Zegveld ALPHA samplers are discussed in section 2.1, together with the ALPHA measurements at other locations. However, the series of measurements with the DELTA denuders from September 2003 to December 2014 is available exclusively for Zegveld, and is therefore discussed separately in this section.

The values of the DELTA denuders cannot be compared directly with the MAN because the DELTA measurements relate to a period of four weeks, and those of the MAN and ALPHA samplers to one month (Braam, 2017). However, the AMOR measured values are available on an hourly basis, which offers the possibility to compare the different measurement methods directly with the AMOR data on the basis of the same sampling period; see Appendix 5 for the method used.

The results of the ALPHA samplers and the (calibrated) Gradko samplers show less outliers than the DELTA denuders (Figure 9). There is a larger spread in measurements of the DELTA denuders.

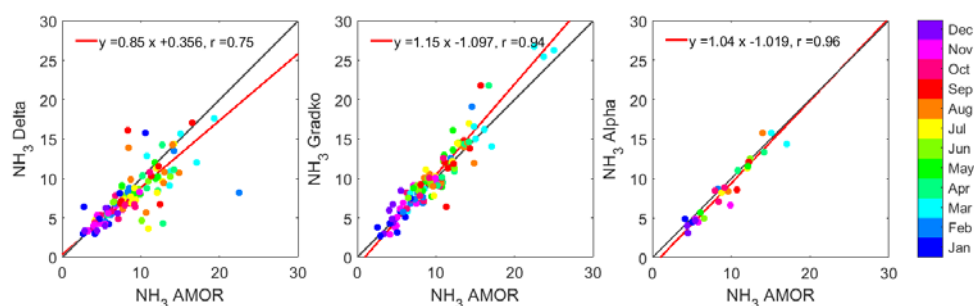


Figure 9: Comparison of the measurements of the DELTA denuder, Gradko samplers and ALPHA samplers with the AMOR data at LML location Zegveld. The hourly values of the AMOR are separately averaged over the time period of the DELTA denuder (four-week period), or the time period of the Gradko and ALPHA samplers (month period). The colours indicate the measured month.

2.3 Comparison with COTAG measurements

The MAN samplers can also be compared with COTAG measurements (Famulari et al., 2010, Stolk et al., 2014). The COTAG measures ammonia concentrations at different heights in order to derive the dry deposition of ammonia. The COTAG measurements are performed during two categories of meteorological conditions. This yields an average concentration per month for both categories separately. At an altitude of 0.8 meters, the average concentration is also measured for the periods when the meteorology falls outside the conditions of the two categories. By combining the measurements from these three

categories, the average ammonia concentration of the month in question can be derived at a height of 0.8 meters. This can be compared with the monthly average values of the Gradko samplers.

In the Bargerveen and in the Oostelijke Vechtplassen, three Gradko samplers have been attached to the COTAG set-up at a height of 0.8 meters since July 2014. There is a fairly good agreement between both measurement techniques (Figure 10). The explained variance is 82% and the offset is only $-0.2 \mu\text{g}/\text{m}^3$.

A disadvantage of this comparison is that it concerns only a small amount of data. However, more COTAG measurements are available. Although their comparison with Gradko samplers is less accurate for various reasons, these measurements also provide - over a larger concentration range - a similar picture of the correspondence between Gradko samplers and COTAG measurements (Appendix 6).

The general conclusion is that the measurements of the Gradko samplers correspond fairly well with those of the COTAG.

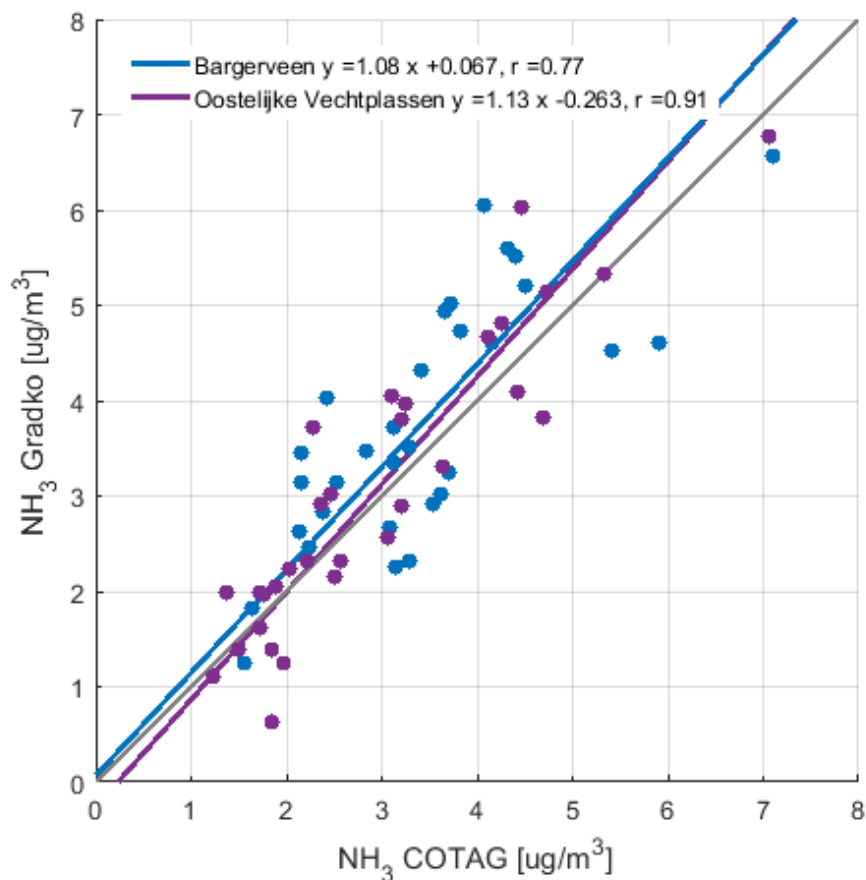


Figure 10: Comparison of the measurements of the COTAG in the Bargerveen and the Oostelijke Vechtplassen with Gradko samplers.

2.4 Comparison with TNO-samplers

In 2002, RIVM commissioned TNO to carry out ammonia measurements at a few dozen locations in the Strabrechtse Heide and Dwingelderveld for a year with its own sampler which is quite similar to the Gradko samplers (Thijssen et al. 1998, Weststrate and Duyzer, 2002). These samplers were calibrated to the AMOR measurements of the LML in a similar way as in the MAN. Almost all current MAN locations in these two areas take place at exactly the same spot or otherwise close to a TNO location from 2002. In the eastern half of the Strabrechtse Heide a few locations have undergone major changes after 2002 due to forestation practices; these have been omitted from this comparison.

Because the weather for the years 2005-2007, the early years of the MAN, on average shows agreement with the year 2002, the TNO measurements were compared with the MAN average for 2005-2007. The TNO measurements are almost identical to those of the MAN (Figure 11). The measured values of the MAN are on average $0.2 \mu\text{g}/\text{m}^3$ lower on the Dwingelderveld and $0.08 \mu\text{g}/\text{m}^3$ lower on the Strabrechtse Heide. Because the measurement periods are several years apart and the measurement locations and local conditions are not entirely identical, the agreement found between the two measurement series is good.

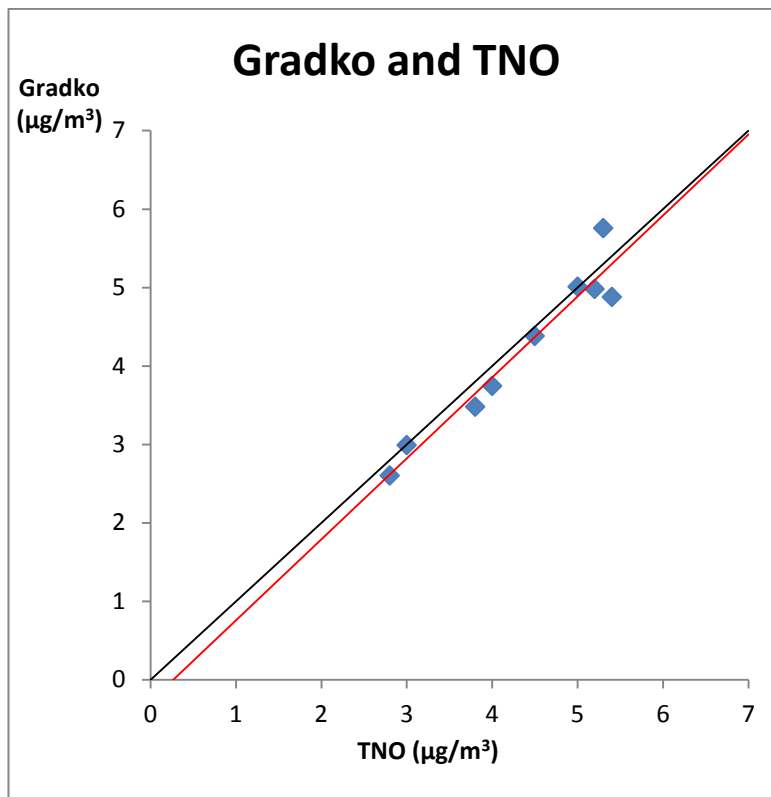


Figure 11: Comparison of the annual mean measurements of TNO in the Strabrechtse Heide and Dwingelderveld in 2002 with Gradko samplers in 2005-2007.

2.5 Other measurement campaigns

There are measurements available from LML location Wekerom with Passam and Radiello samplers in addition to the Gradko samplers and the current LML reference instrument; the mini-DOAS. These measurements started in July 2016 and have still yielded too few data for a meaningful comparison. Those available do not indicate a clearly better performance of the Passam or Radiello samplers compared to the calibrated Gradko measurements. Both samplers give a concentration that is about 25% lower than the reference instrument.

At an international comparison study at Whim Bog near Edinburgh from 16 August to 11 October 2016, several samplers were attached next to each other in the field: Gradko, Radiello, Passam, ALPHA, FERM and IVL (Stephens et al. 2017). The measurement period was too short for detailed conclusions, however the collaborating laboratories, including RIVM, and the tested samplers all performed reasonably well. The RIVM and Gradko measurements themselves were very similar. The logistical handling, which was more extensive with the Gradko samplers used by the RIVM, therefore had little effect on the RIVM measurements. The observed noise in the Gradko samplers was not larger than that of other samplers, only the ALPHAs scored slightly better, in accordance with our observations described in 2.1. Of all the samplers tested, the Gradko samplers were still closest to the results of the AiRmonia reference instrument.

3 The influence of meteorology on the measurement results

The measuring principle of the Gradko samplers is based on molecular diffusion. This diffusion takes place after ammonia has entered the sampler through the filter membrane until the ammonia comes into contact with the absorbing liquid that finally binds ammonia. From the ammonia concentration in the absorption liquid, the concentration in the air over the measuring period is calculated via a fixed conversion factor. Molecular diffusion, however, depends on various conditions, including temperature and air pressure. This means that the measured value is influenced by the meteorological conditions during the measurement period. Temperature, radiation and relative humidity show clear variation through the seasons (Appendix 7). The Gradko measurement value can therefore deviate from the actual ammonia concentration in a fairly fixed seasonal pattern.

However, the Gradko measurements are calibrated per month on the AMOR measurements and from autumn 2015 onwards on mini-DOAS measurements (Volten et al., 2012, Berkhout et al., 2017). The mini-DOAS instrument uses an optical method which is independent of meteorological conditions. The AMOR measures the ammonia concentration via the conductivity, which is temperature-dependent, but this is corrected in the measuring instrument itself. The quantity of sampled air is measured with a mass flow meter, so the final measured value of the AMOR, reported for a fixed volume at 20 °C and 1 atmosphere, is fairly independent of meteorology.

We thus assume that the AMOR measurement is virtually independent of the meteorological conditions and that the monthly calibration of the Gradko measurements on the AMOR data is correct. It can thus be expected that the calibrated Gradko measurement will also be almost independent of meteorology. The effect of meteorology is then only present in the calibration constants. This is what is tested in this chapter.

In addition to the influence of meteorology on the systematic deviation of the measurements, the noise in the measurements could also depend on meteorology. However, no clear seasonal pattern caused by meteorology appears to be present in the mutual variation within the triplicate samplers (Appendix 8). Given the large seasonal variation in meteorological conditions and the absence of seasonal patterns in the variation within triplicate samplers, only the systematic deviation in Gradko samplers and calibration is examined. Meteorological influences on the noise in the measurements are therefore not considered.

The effect of meteorology was investigated by pairing the measured values of the AMOR and the Gradko samplers. A detailed explanation of the analysis is given in Appendix 9. In the ratio AMOR / uncalibrated Gradko, an annual recurring pattern is recognizable over the period 2005-2016 with a minimum in winter and a maximum in summer (image 12 at the top). The ratio is clearly influenced by various meteorological parameters, especially the temperature (Figure 12,

middle and bottom). The analyses were carried out with meteorology data from the Royal Netherlands Meteorological Institute (KNMI) station De Bilt. After calibration, the meteorological influence virtually disappeared (Figure 13). A further analysis of meteorological influence on the measurement results of the individual LML locations can be found in Appendices 9 and 10. The effect of the calibration at different concentration levels is analysed in Appendix 11.

The calibration has thus effectively eliminated the meteorological influence on the measurement by Gradko samplers. This meteorological influence must then be reflected in the calibration parameters. A Fourier analysis was performed, indicating that there is an annual variation in the calibration parameters (Appendix 12). This can be explained by the strong seasonal cycle in the temperature in combination with the influence of temperature on the molecular diffusion in the Gradko sampler.

As expected, the calibration constants show some seasonal variation, apparently caused by several meteorological parameters. In the first years, random fluctuations seem to predominate. In the final years, the seasonal variation is less clearly visible. The offset (figure 14) has a peak in the summer period and lowest values in the winter period. Temperature and relative humidity appear to have the strongest correlations with the offset. For the slope, the season variation is less clear, with a maximum in winter (Figure 15). Here, all the investigated meteorological parameters have some correlation with the slope, all more or less to the same degree. Together, Figures 12-15 demonstrate that the calibration successfully eliminates the meteorological influences on the Gradko measurements.

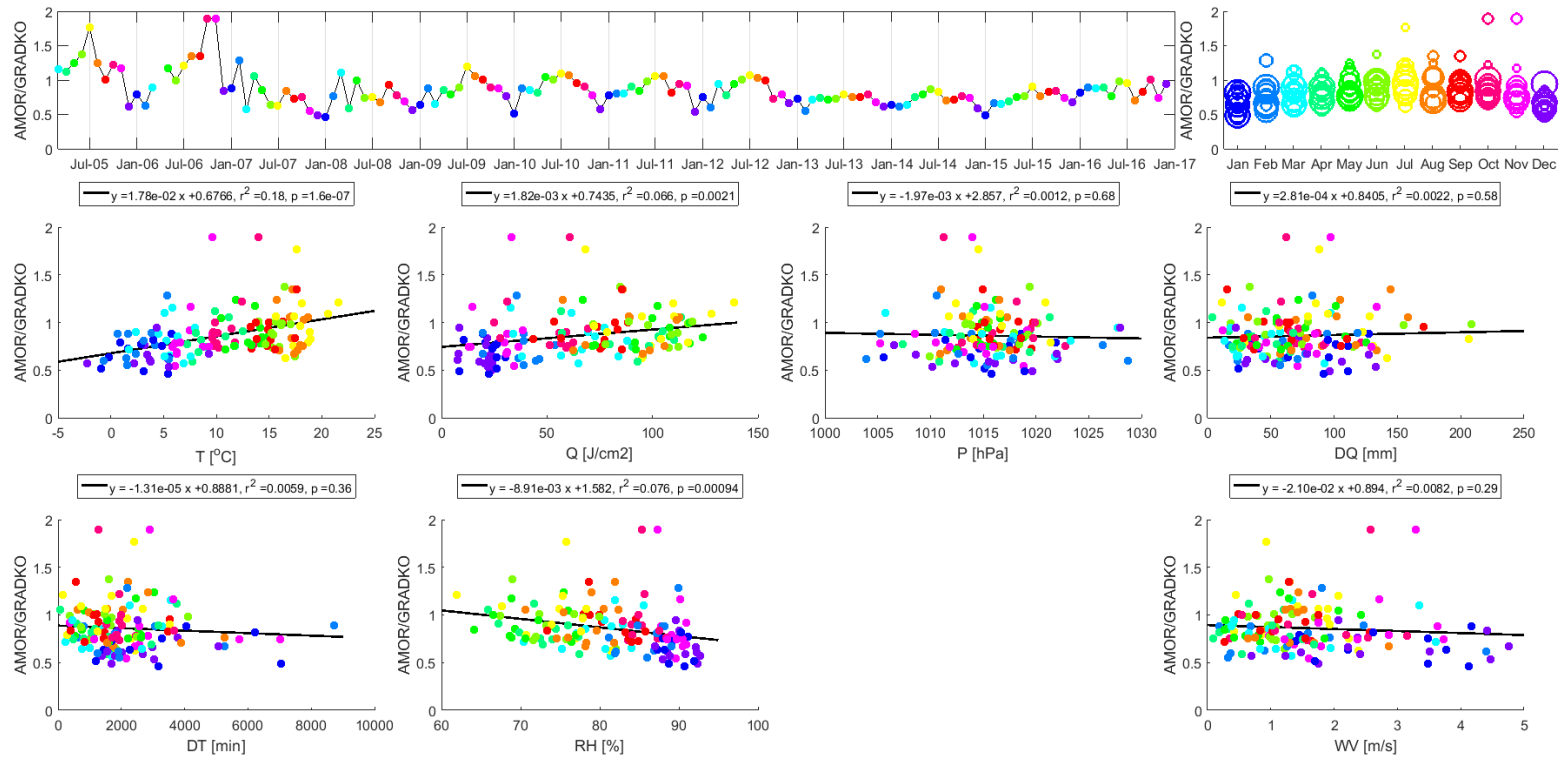


Figure 12: The influence of meteorological parameters on the ratio AMOR / uncalibrated Gradko, averaged over all LML locations per month. At the top left, the sequence with proportions on a timeline; top right the season with the largest bulbs indicating the most recent years. Underneath the meteorological parameters T (Temperature, °C), Q (Radiation, Joule/cm²), P (Air pressure, hPa), DQ (Precipitation amount, mm), DT (Precipitation duration, minutes), RH (Relative humidity, %) and WV (Wind speed, m/s). The 2016 data are based on the mini-DOAS instead of the AMOR as a reference instrument, the measured values of that year have not yet been finalized.

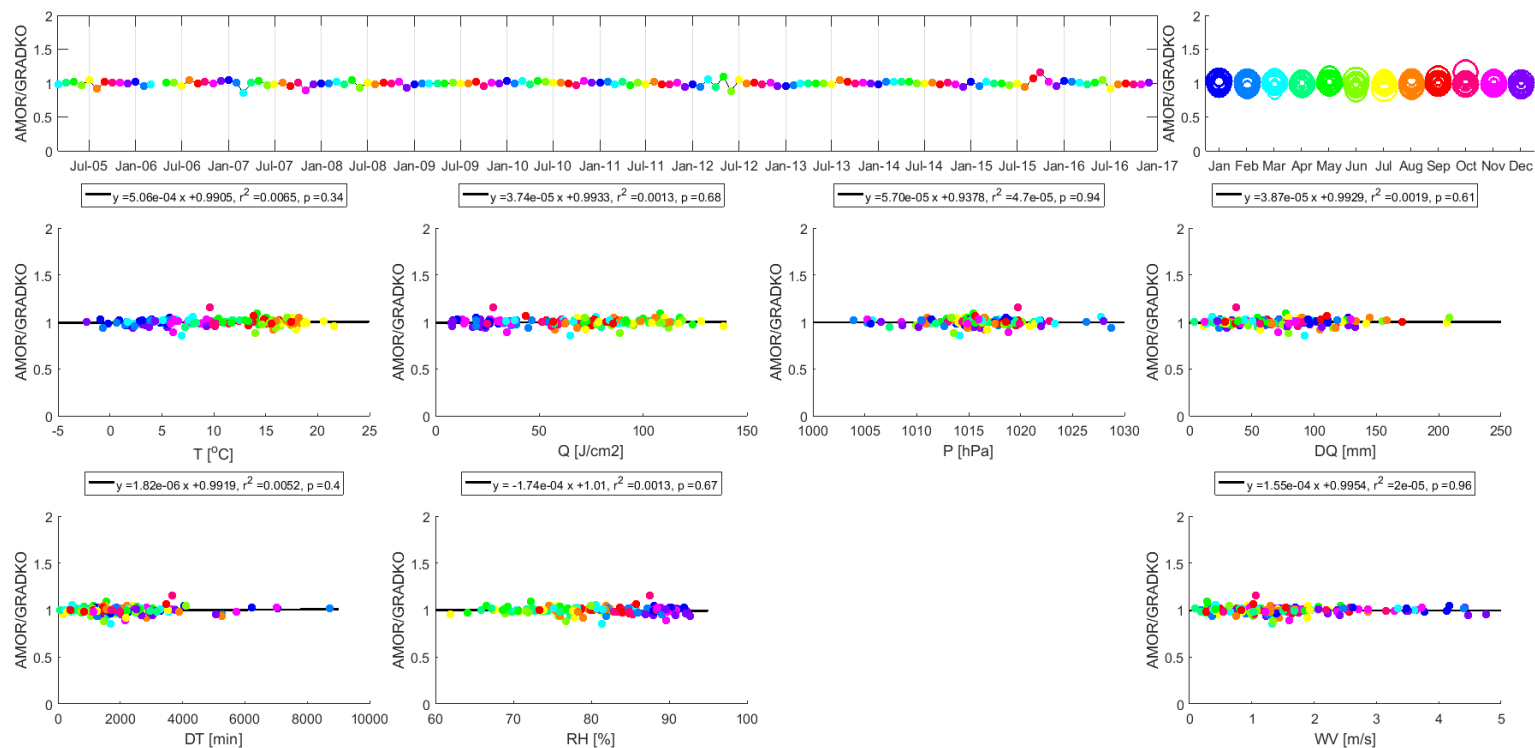


Figure 13: The influence of meteorological parameters on the ratio AMOR / calibrated Gradko, averaged over all LML locations per month. At the top left, the sequence with proportions on a timeline; top right the season with the largest bulbs indicating the most recent years. Underneath the meteorological parameters T (Temperature, °C), Q (Radiation, Joule/cm²), P (Air pressure, hectoPascal), DQ (Precipitation amount, mm), DT (Precipitation duration, minutes), RH (Relative humidity, %) and WV (Wind speed, m/s). The 2016 data are based on the mini-DOAS instead of the AMOR as a reference instrument, the measurement values of that year have not yet been finalized.

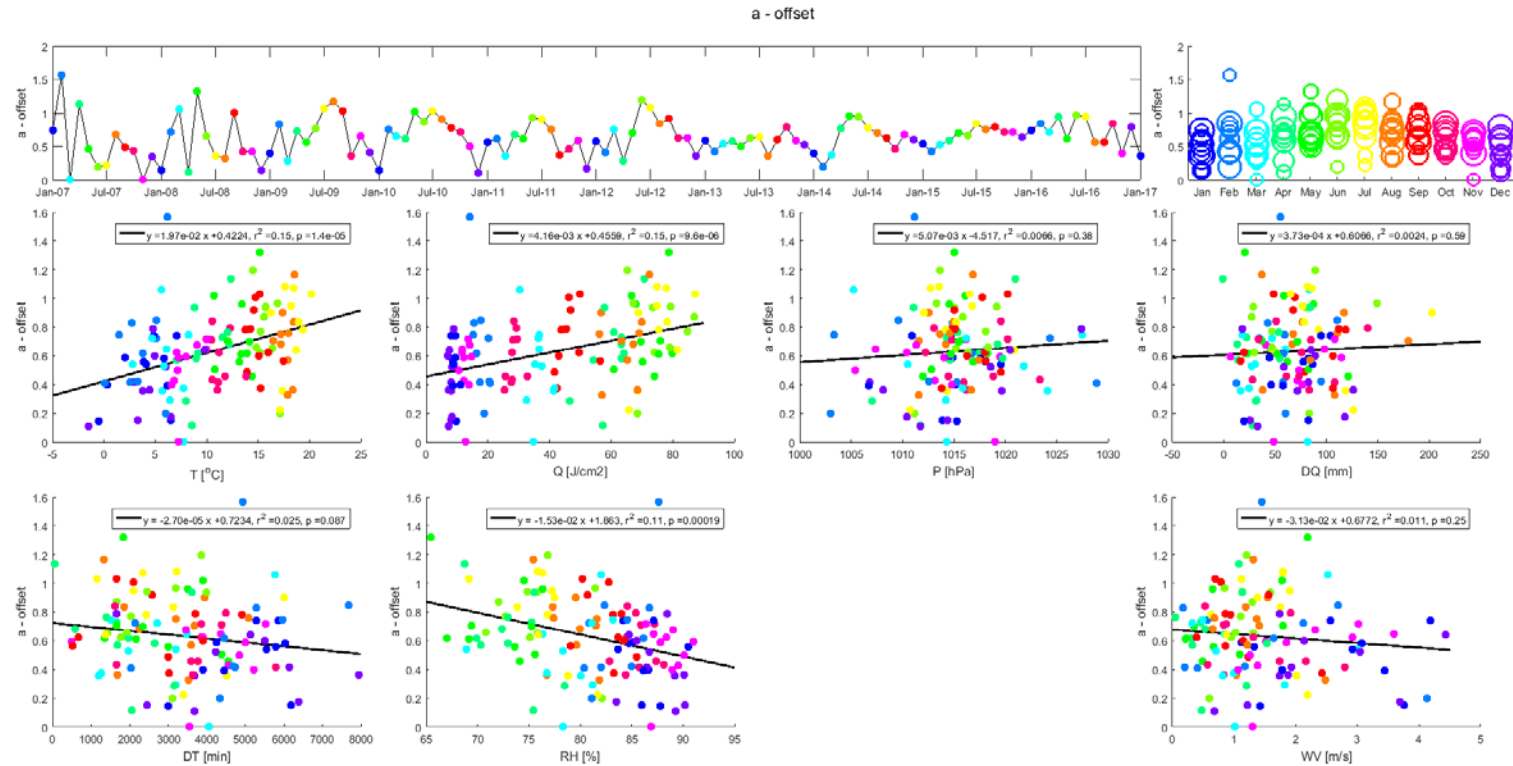


Figure 14: The influence of meteorological parameters on the offset of the calibration line. At the top left, the sequence with proportions on a timeline; top right the season with the largest bulbs indicating the most recent years. Underneath the meteorological parameters T (Temperature, °C), Q (Radiation, Joule/cm²), P (Air pressure, hectoPascal), DQ (Precipitation amount, mm), DT (Precipitation duration, minutes), RH (Relative humidity, %) and WV (Wind speed, m/s). The 2016 data are based on the mini-DOAS instead of the AMOR as a reference instrument, the measurement values of that year have not yet been finalized.

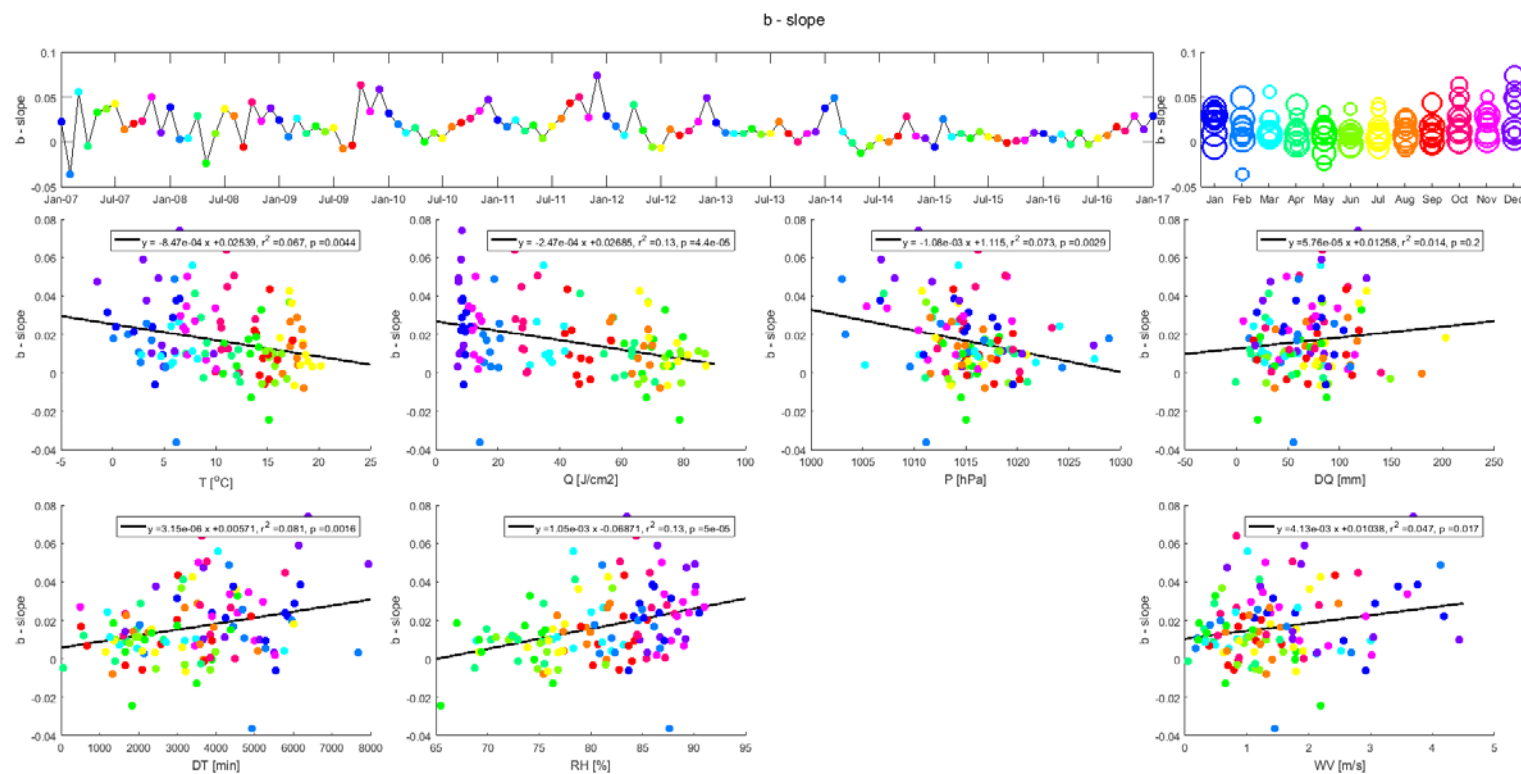


Figure 15: The influence of meteorological parameters on the slope of the calibration line. At the top left, the sequence with proportions on a timeline; top right the season with the largest bulbs indicating the most recent years. Underneath the meteorological parameters T (Temperature, °C), Q (Radiation, Joule/cm²), P (Air pressure, hectoPascal), DQ (Precipitation amount, mm), DT (Precipitation duration, minutes), RH (Relative humidity, %) and WV (Wind speed, m/s). The 2016 data are based on the mini-DOAS instead of the AMOR as a reference instrument, the measurement values of that year have not yet been finalized.

4 The quality of the sampler exchange by volunteers and site managers

4.1 The reliability of volunteers with the use of Gradko samplers

An important quality aspect is uncertainty in the method added by the efforts of volunteers and site managers. Except during the period with the use of ALPHA samplers in addition to the Gradko samplers, no independent measurements are available that provide insights into this. However, the influence of the behaviour of the exchanger can be somewhat verified on the basis of the spread in the results of the triplicates. Ideally these deliver the same value three times each time.

The standard deviation in the triplicate measurements is a measure of the reproducibility of the Gradko measurements. This reproducibility can be reduced, amongst others, by careless handling of the samplers. Examples of this are the improper closure or suspension of the samplers, or dirt that ends up on the samplers during the exchange. Reproducibility can also be adversely affected by external factors around the measuring point, for example by bird droppings.

The variation in the measurements is calculated as the relative standard deviation in the annual mean values, because these annual averages form the basis for trend series and for comparisons with model calculations. In all nature reserves, at least one triplicate is present from 2011 onwards. Of these, annual mean values have been derived for the period 2012-2014.

The relative standard deviation is shown as a percentage of the triplicate mean values (Figure 16). The triplicates are ranked by increasing triplicate average. For the lowest triplicate averages, on the left of the figure, the standard deviation in terms of percentage is more than one and a half times higher than for the highest triplicate measurements.

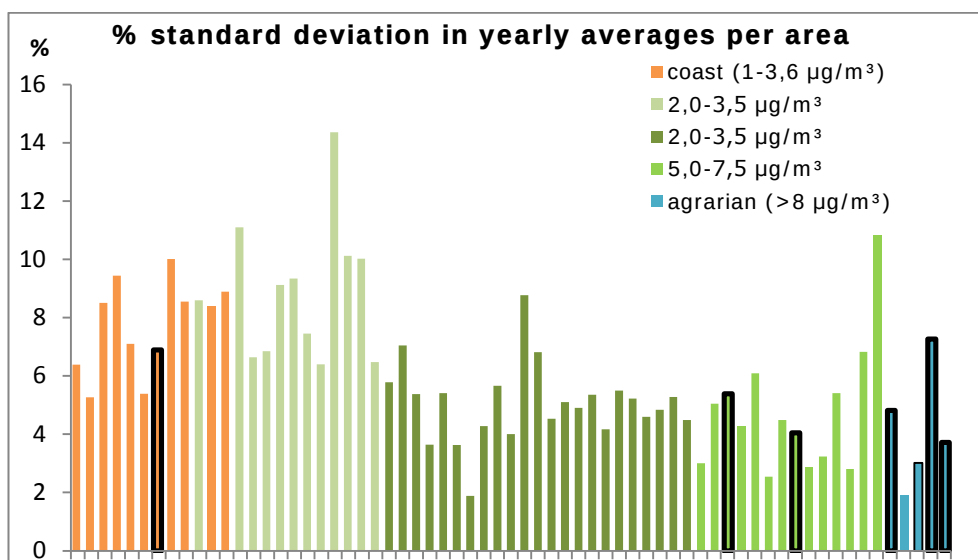


Figure 16: Comparison of the standard deviation in the triplicate values per nature area with those at the LML locations (black outlined).

The average inaccuracy observed by the MAN site managers and volunteers is not significantly different from that of the LML observations (Figures 16 and 17). The handling by the volunteer employees in the MAN, including the storage period at the office or the work site of the site manager and the dispatch via the post, therefore have no significant influence on the reproducibility of the samplers.

As stated before, other factors than the handling of the samplers can also influence the standard deviation of the triplicates. This analysis does not in principle exclude the possibility of systematic differences between the LML exchange and those of the MAN volunteers, but to give a definite answer requires a very different and much greater measurement effort. The constant reproducibility gives confidence in the way in which the volunteers and site managers handle the samplers on average in the MAN. It should be noted, however, that since the end of May 2010, at LML locations 131, 538 and 929 the exchange has been done by local assistants instead of RIVM personnel.

Moreover, the estimation of the standard deviations in this analysis is not very accurate because, for the entire measurement network, only three years of measurements have been available since the end of 2011. A triplicate measurement yields three annual averages annually, whereas the dataset only contains nine measured values per nature reserve. A more extensive investigation into the standard deviation based on triplicate measurements at the LML locations, available since 2005, makes it plausible that the dataset does not offer sufficient accuracy to compare individual changers, but that a comparison between the LML exchangers as a group and the group of MAN voluntary employees is possible (Appendix 13). The fairly large deviation between the LML and the MAN volunteers for the agrarian category will partly be due to the very small number of MAN locations in the agrarian category.

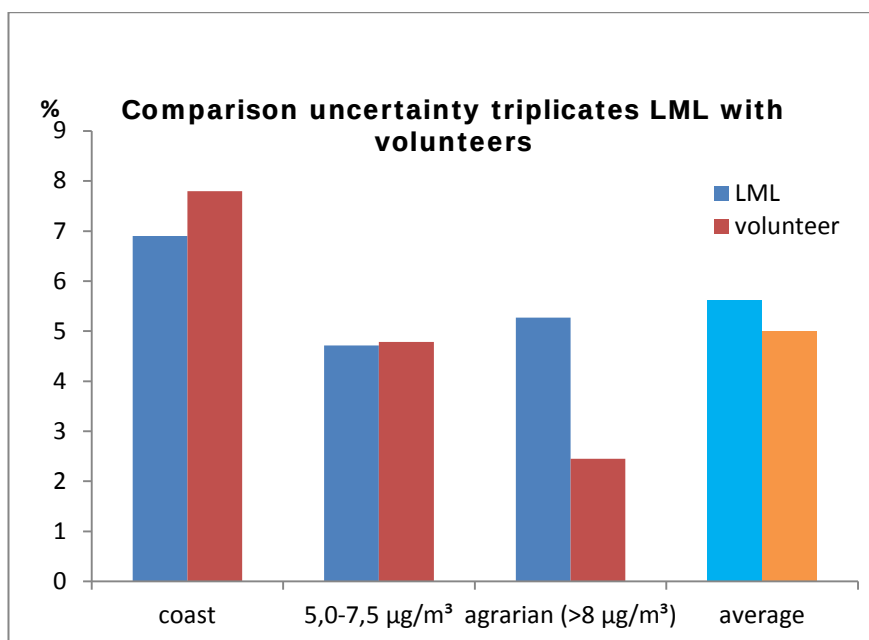


Figure 17: Comparison of the standard deviation in the triplicate values of the MAN with those at LML locations.

4.2 The reliability of volunteers with the use of ALPHA samplers

The Gradko and ALPHA samplers were simultaneously switched by 7 LML and MAN employees over a period of 1 (nature reserves) to more than 2 years (LML locations). The ALPHA samplers are more vulnerable when they are replaced due to their less robust construction. Also the way of suspension sometimes caused problems by samplers, as they were blown away by the wind.

The results show a high drop among the ALPHA measurements (Figure 18). Of the Gradko samplers, 2 - 10% were lost over this period whereas 20 - 90% of the ALPHA measurements were lost. From the holiday period, June-July 2012, not one valid ALPHA measurement is available from the three MAN nature reserves. However, in the holiday months, the MAN measurements are also always of a lesser quality as less experienced people are in charge.

The measurement locations in Terschelling, Meyendel and Zwanenwater are part of the MAN, the other locations are part of the LML. After a few months of measuring, the exchangers in Terschelling, Meyendel and Zwanenwater were re-instructed for the way in which the ALPHA samplers had to be exchanged, but without any substantial improvement except for a short-term improvement at the six locations in Terschelling.

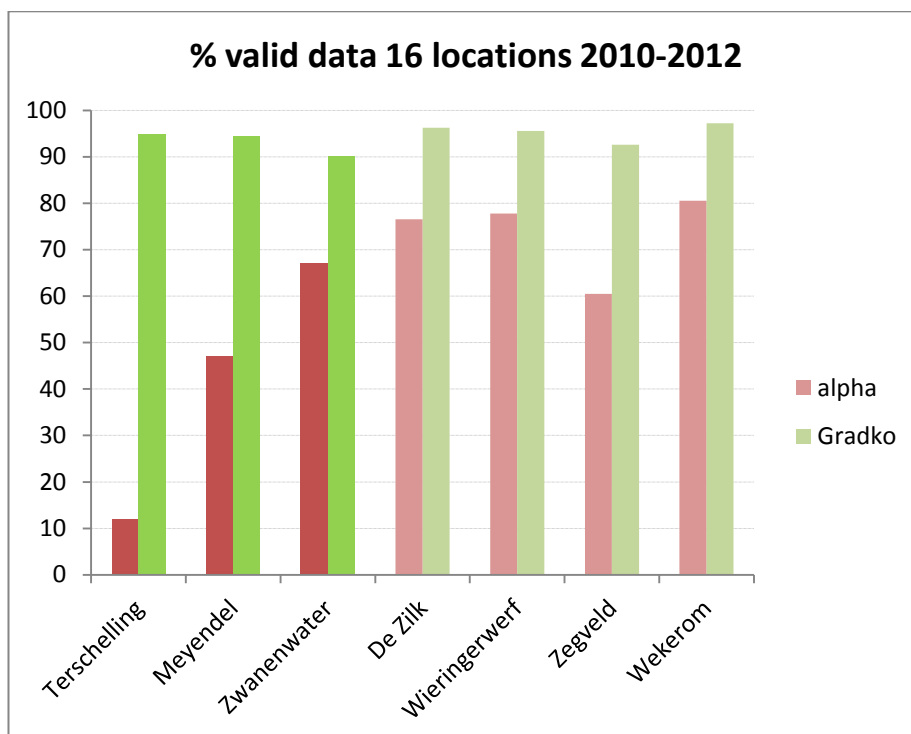


Figure 18: The percentage of valid data from Gradko and ALPHA samplers in 7 different nature areas and LML locations.

The exchangers in Meyendel and Zwanenwater are among the above-average performers in the MAN, and the sampling in Terschelling took place during that period at a level that roughly corresponds to the average sampling in the MAN over time. The dropout in a large-scale

application of ALPHA samplers may even be worse than what has been observed for these three MAN areas.

In addition, it is important to note that the ALPHA samplers attract much more attention than the freely suspended Gradko samplers (Figure 19) because of their fairly large housing in the field. In the MAN network, a small part of the Gradko measurements have been lost due to vandalism. With a large-scale application of ALPHA samplers this is expected to become a greater problem.



Figure 19: The Gradko sampler (left) and the housing of the ALPHA sampler (right) in the Meyendel bar.

The MAN is dependent on the voluntary cooperation from site managers and volunteers. The quality of the services they provide is often at a different level than that of qualified laboratory staff. This should be taken into account when using this type of resource for sampling. The large-scale deployment of samplers, such as in the MAN, therefore benefits from a simple and robust design that can be performed not only by these volunteers, but also by other people in vacation periods and in cases of illness. The required actions when changing Gradko samplers are much easier than those with other common types of ammonia samplers. The dropout observed in the application of ALPHA samplers in this study gives an indication of what can be expected if other samplers than those of Gradko are used in the monitoring network.

5 Conclusions

In the MAN-network of nearly 280 locations in nature reserves, the ammonia concentrations are measured using Gradko samplers that are exchanged every month. Important advantages of these samplers are their compactness, inconspicuousness and simple exchange. In addition, they are also less expensive than other commercially available samplers. In all these aspects they are more attractive than alternative samplers. A disadvantage is that Gradko samplers are less accurate. This disadvantage is overcome by calibrating the Gradko samplers in the MAN measurement network to six reference instruments localized throughout the Netherlands.

Without calibration, the measurements made by the Gradko samplers are systematically too high, especially at low concentrations. After calibration, there is no substantial systematic difference with respect to the reference instrument. The noise in the measurements is also reduced as the calibration procedure implicitly corrects for the meteorological influence on the Gradko measurements.

A comparison with various alternative measurement techniques shows that the calibrated Gradko measurements are comparable with state-of-the-art passive samplers such as the ALPHA sampler. A disadvantage of the Gradko sampler is that it still shows slightly more noise after calibration than, for example, the ALPHA sampler, but this shortcoming disappears when averaging several measured values i.e. in space or time. As a result, this technical noise no longer plays a role in annual mean values and trend determination.

Because the MAN makes use of the efforts of volunteers and site managers, a simple and robust design is of great importance. The Gradko samplers appear to be fit for this purpose in that respect.

An important feature of the Gradko samplers is their small size. This not only simplifies the shipping procedure, which is important for the volunteer, but the Gradko sampler is much less noticeable in the field than the alternatives. This is an important aspect as nature reserves in the Netherlands are crowded, which can easily lead to violation of the samplers.

6 Literature

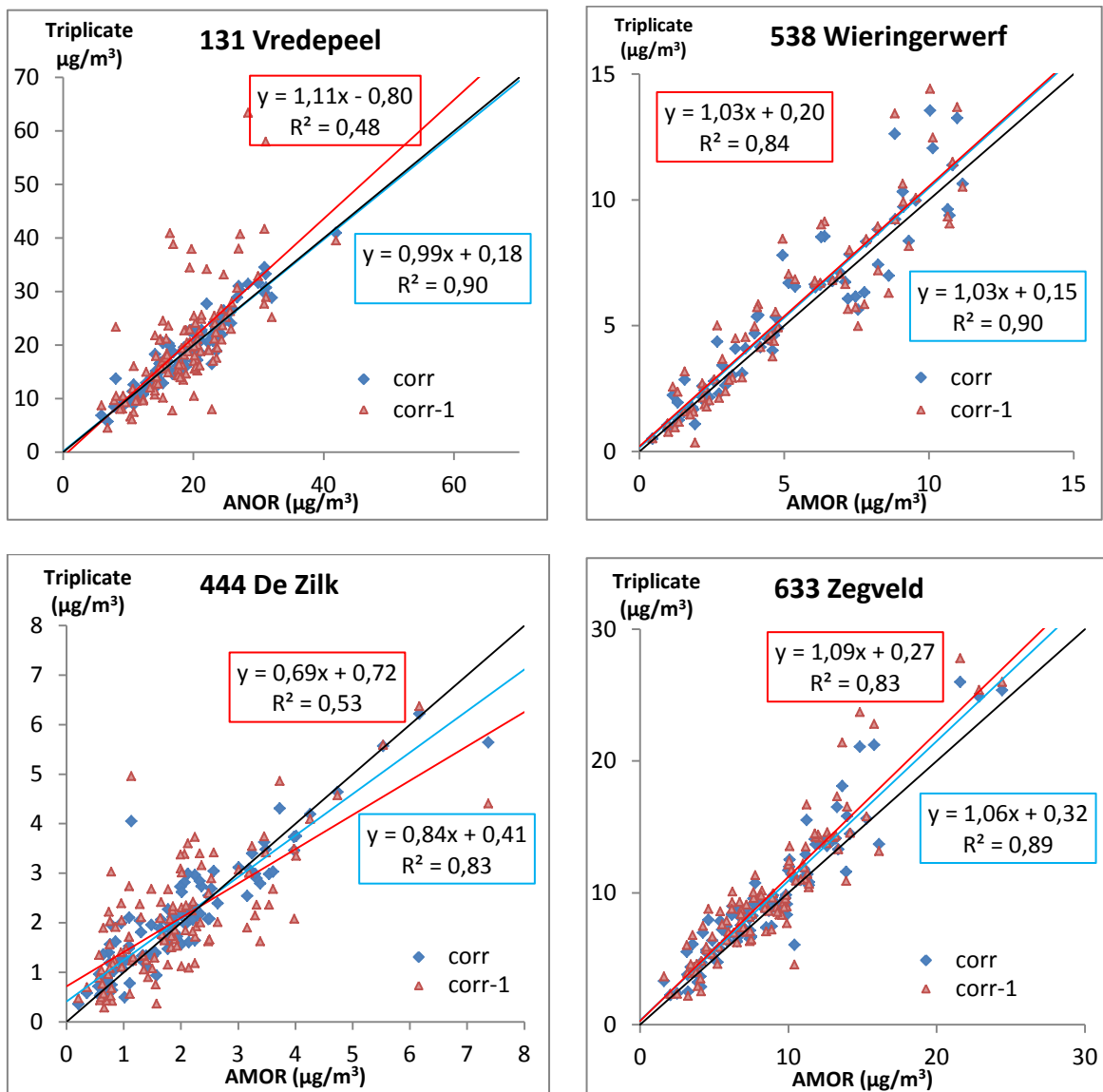
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Appendix 1: Comparison of calibrated Gradko samplers with AMOR per LML location

For each location, the triplicate average of the calibrated Gradko measurements is plotted against the AMOR measurement value. The calibration was performed in two ways: 1) a calibration with application of all LML locations ("corr") as the standard is applied within the MAN, and 2) a calibration where one LML location is not included, namely that location whose Gradko values are compared with the AMOR ("corr-1"). The line "Y = X" is shown in black, the regression line and the associated formula and explained variance are shown for both calibration methods.



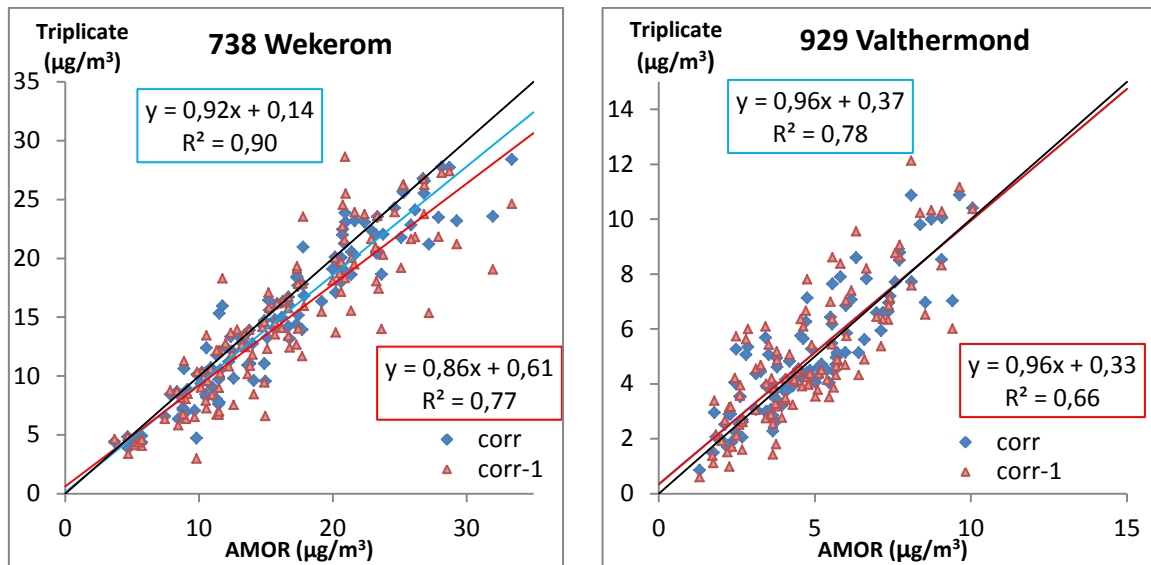


Figure B1.1: Calibrated triplicate Gradko measurements versus AMOR values, by use of two different calibration methods.

Appendix 2: Aggregate data comparison Gradko with AMOR

The deviation between the uncalibrated individual Gradko samplers and the AMOR measurements is quite large, on average 1.5 to 2 $\mu\text{g}/\text{m}^3$ over the entire data range (Figure B2.1). After calibration, the average deviation is much smaller, 0.20 - 0.25 $\mu\text{g}/\text{m}^3$ for the corr-1 method, and about 0.20 $\mu\text{g}/\text{m}^3$ for normal calibration. All deviations indicate a small systematic overestimation by the calibrated Gradko samplers.

This image is more variable per location. The deviations are relatively small after calibration on the three sites with lower concentrations, and vary from 0.1 to 0.3 $\mu\text{g}/\text{m}^3$. For the locations with higher concentrations, Zegveld, Wekerom and Vredepeel, the deviation is usually 1 $\mu\text{g}/\text{m}^3$ on average. After calibration, the measured values at Wekerom are underestimated by approximately 1.5 $\mu\text{g}/\text{m}^3$ by the Gradko samplers; the other locations are overestimated.

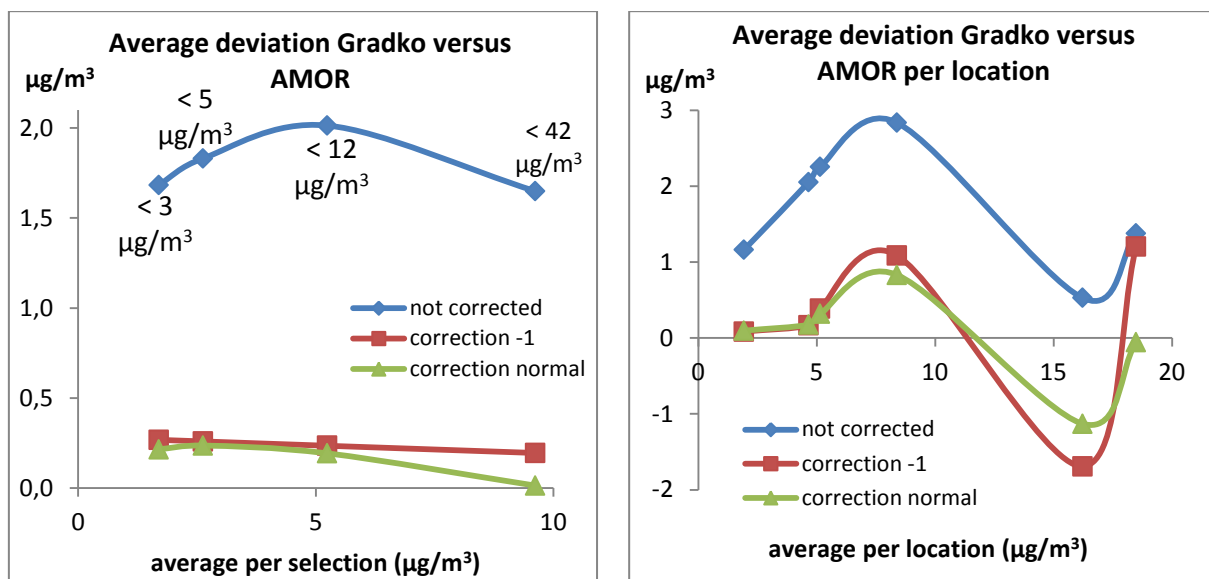


Figure B2.1: Average deviation individual samplers Gradko versus AMOR values. Left for concentrations of 0-3, 0-5, 0-12 and 0-42 $\mu\text{g}/\text{m}^3$, right per AMOR location.

The offset indicates whether there is systematic under- or overestimation in the Gradko data at low concentrations. Without calibration, the offset is high, around 2 $\mu\text{g}/\text{m}^3$. Also after calibration, this cut-off of the Y-axis is almost always a positive value, which indicates that the calibrated Gradko values have a tendency to slightly overestimate the actual value at low concentrations (Figure B2.2). The axis cut is usually a few tens of percent higher in the corr-1 calibration when compared to the normal calibration; for individual locations there is more variation in the results of both methods. Noteworthy is the strong negative value of -0.8 $\mu\text{g}/\text{m}^3$ for the highest location (131 Vredepeel) at method corr-1.

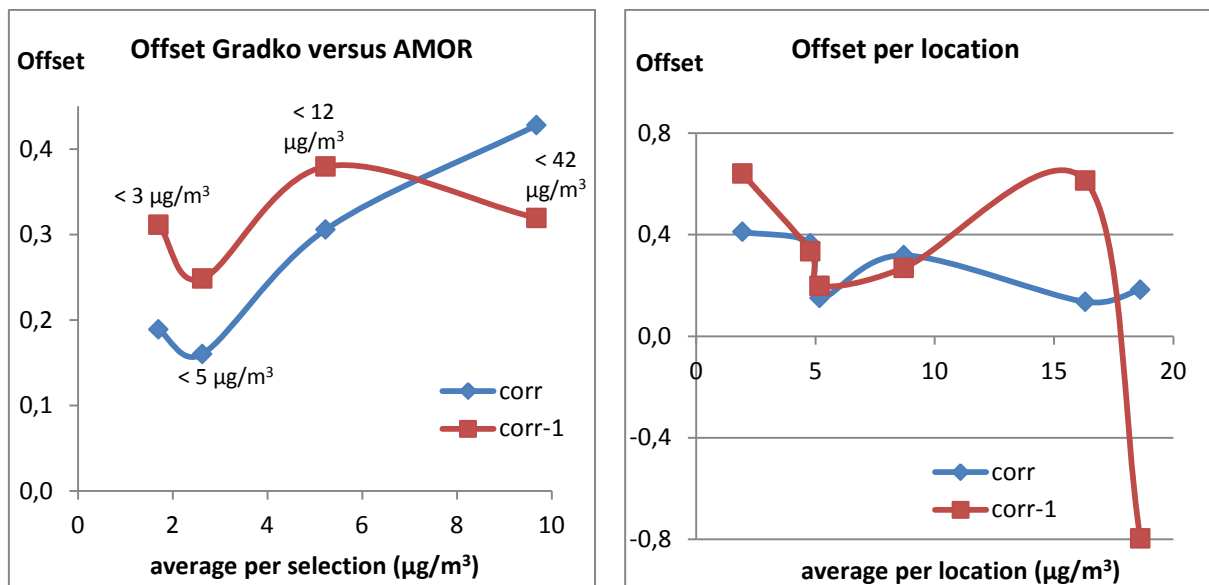


Figure B2.2: offset in $\mu\text{g}/\text{m}^3$. Left for 4 selections of data, right per AMOR location.

The standard deviation between individual Gradko observations and the AMOR data is around $3 \mu\text{g}/\text{m}^3$ for uncalibrated values (Figure B2.3). This is approximately $1 \mu\text{g}/\text{m}^3$ for calibrated values less than $5 \mu\text{g}/\text{m}^3$ and it rises to $2 \mu\text{g}/\text{m}^3$ for calibrated values around $10 \mu\text{g}/\text{m}^3$.

The standard deviation between Gradko data and AMOR data improves after calibration, but this is mainly due to the strong decrease in the systematic overestimation after calibration. Around a measured value of $2 \mu\text{g}/\text{m}^3$, the standard deviation for individual uncalibrated sampler values is around $2.5 \mu\text{g}/\text{m}^3$; for the two calibration methods this is 0.9 to $1.1 \mu\text{g}/\text{m}^3$. On average over the range of $0\text{--}12 \mu\text{g}/\text{m}^3$ (not calibrated) the standard deviation is $3.1 \mu\text{g}/\text{m}^3$; for the two calibration methods this is 1.5 to $2.0 \mu\text{g}/\text{m}^3$. For location Vredepeel, with the highest ammonia concentrations, however, the corr-1 method adds uncertainty to the measurements. The normal calibration always performs slightly to much better than the corr-1 method.

These standard deviations are clearly higher than the noise within the Gradko measurements themselves. If the standard deviation within the Gradko measurements is related to the Gradko average instead of to the AMOR data, it is about $0.9 \mu\text{g}/\text{m}^3$ instead of $1.5\text{--}2.0 \mu\text{g}/\text{m}^3$ over the range of $0\text{--}12 \mu\text{g}/\text{m}^3$. This difference probably arises, for a small part, from the noise in the AMOR data averaging over 6.8% over the entire AMOR range (Lolkema et al. 2105) which in the lower MAN range amounts to about $0.4 \mu\text{g}/\text{m}^3$. Together, the noise in the Gradko values and the AMOR values give a noise of about $1 \mu\text{g}/\text{m}^3$. This means that the corr calibration method increases the total uncertainty by about half to $1.5 \mu\text{g}/\text{m}^3$, and that the corr-1 method doubles the instrumental uncertainty to $2 \mu\text{g}/\text{m}^3$.

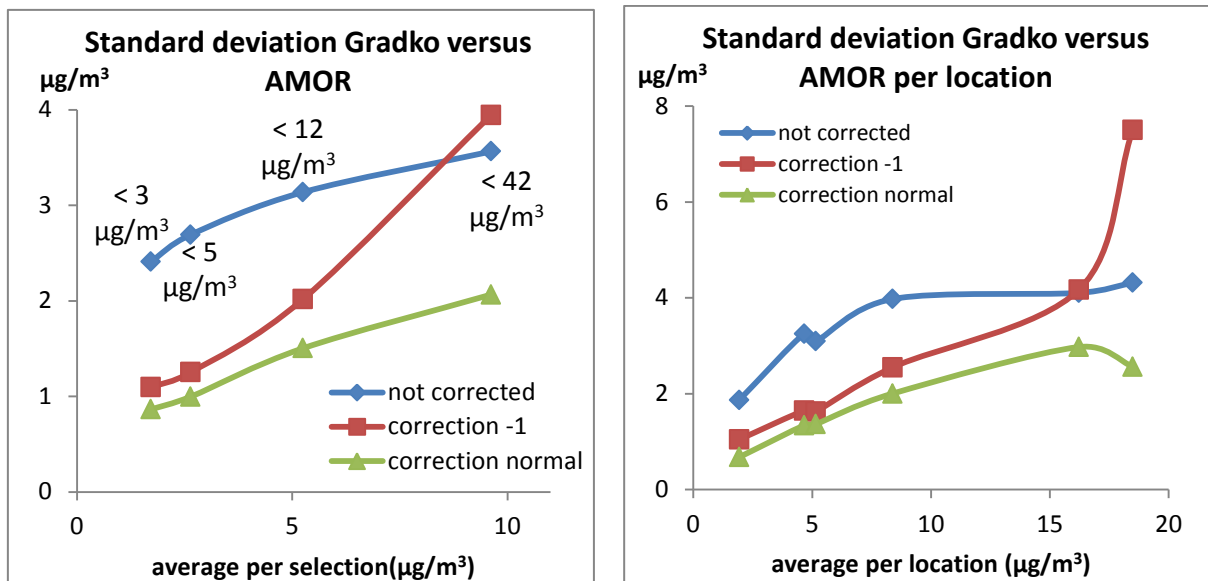


Figure B2.3: Standard deviation of individual samplers Gradko versus AMOR values. Left for 4 selections of data, right per AMOR location.

The slope of the regression lines of the Gradko data with respect to AMOR data is almost always close to the 1: 1 line, which indicates that the results of both calibration methods are, on average, close to the dynamics in the reference measurements (Figure B2.4). In the MAN main range of 0-10 $\mu\text{g}/\text{m}^3$, the slope deviates substantially only from the 1: 1 line at the lowest concentrations, namely that of the Zilk measuring point in the Kennemerduinen.

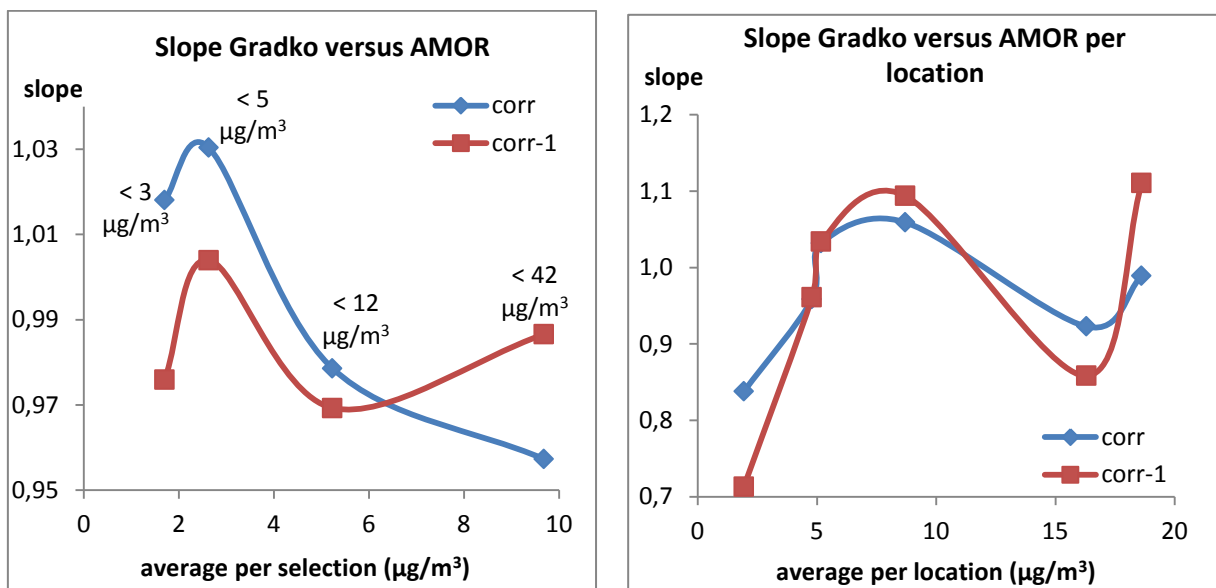


Figure B2.4: The slope of Gradko triplicate averages versus AMOR values. Left for 4 selections of data, right per AMOR location.

Appendix 3: Reproducibility Gradko and ALPHA measurements per LML location

The reproducibility of the Gradko measurements at the individual LML locations is shown by plotting the individual sampler values against their triplicate average. The black line shows the trend line through the points.

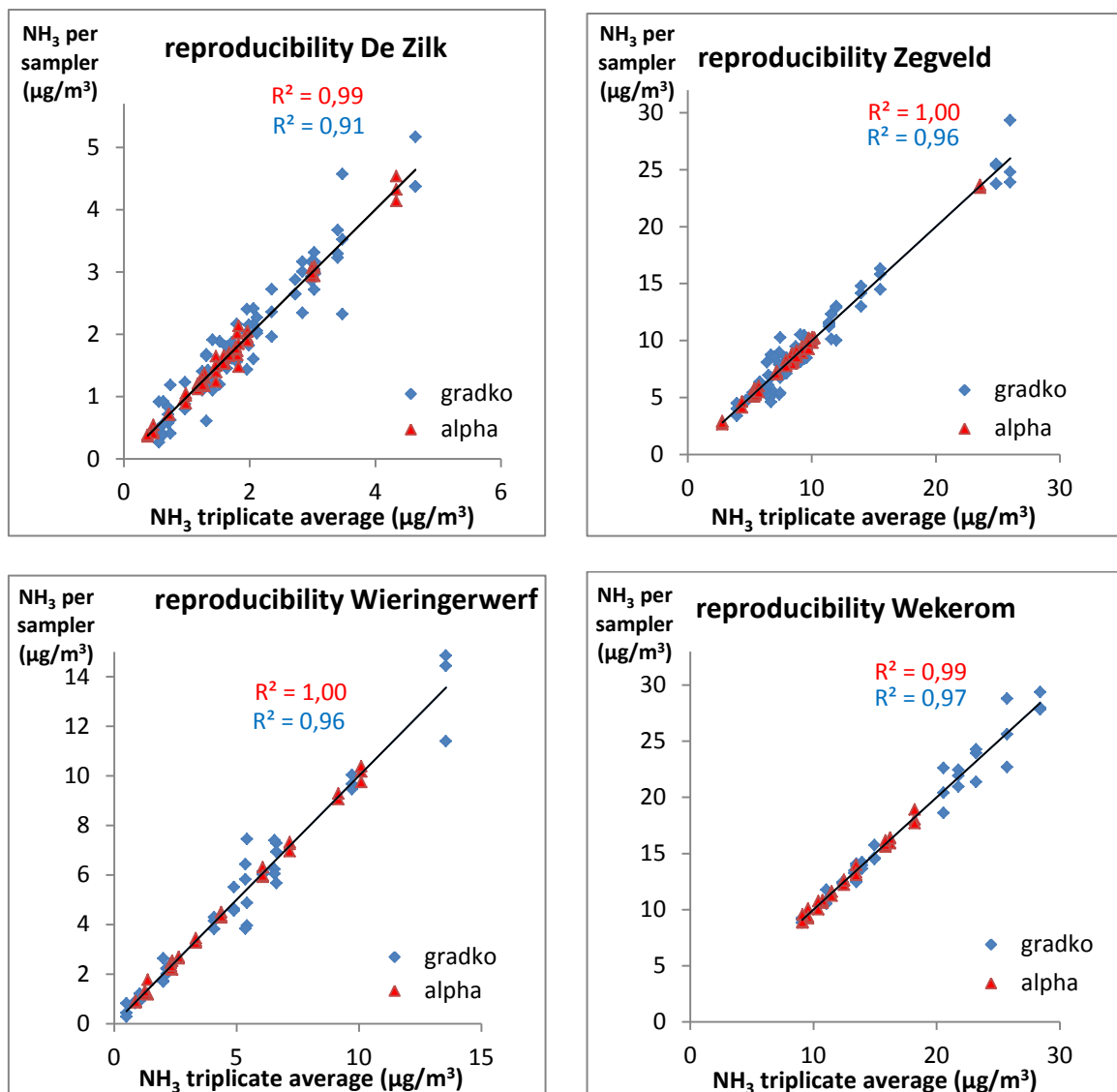


Figure B3.1: Reproducibility of Gradko and ALPHA measurements at LML-sites.

Appendix 4: Gradko and ALPHA measurements per LML location compared to AMOR data

To determine the samplers' quality, in addition to the noise, the presence of systematic deviations in the deviation of the 1: 1 line in the slope and the cut of the Y-axis are required. Both depend on the measurement path under consideration. As shown in Figure 6, the ALPHA scores badly for the concentration range above $15 \mu\text{g}/\text{m}^3$, but well below $10 \mu\text{g}/\text{m}^3$. For this reason, the slope of the calibrated Gradko samplers and the ALPHA samplers with respect to the AMOR data is given here, both for individual samplers and for the triplicate average, for the measurement ranges 0-30 $\mu\text{g}/\text{m}^3$, 0-10 $\mu\text{g}/\text{m}^3$ and 0-5 $\mu\text{g}/\text{m}^3$ (image B4.1).

There are two significantly different triplicate values of the Gradko samplers belonging to AMOR values of almost $5 \mu\text{g}/\text{m}^3$ at the Zegveld location. At this location, clearly different sampler values were found more often over the entire MAN period (2005-2014). Because these two values strongly affect the slope and offset of the Gradko samplers in the range of 0-5 $\mu\text{g}/\text{m}^3$, for this range the slope and offset of the ALPHA and Gradko are shown including and excluding these two extreme values.

If the two different triplicates at Zegveld and the ALPHA measurements above $10 \mu\text{g}/\text{m}^3$ are not included, the slope is always fairly close to the 1: 1 line for both samplers. Especially the Gradko values match the 1: 1 line in the range 0-10 $\mu\text{g}/\text{m}^3$ well after discarding the two Zegveld extremes (slopes of 0.98, 1.00, 1.00 and 1.02).

The offset is especially important at low concentrations, because there it contributes most in relative terms to the deviation from the reference value of the AMOR. Over the entire range of 0-30 $\mu\text{g}/\text{m}^3$ there is a substantial cut-off of the Y-axis in the Gradko samplers, namely 0.5-0.6 $\mu\text{g}/\text{m}^3$, but this is mainly determined by the higher values in the series, where this axial cut-off hardly adds any additional uncertainty. In the range 0-10 $\mu\text{g}/\text{m}^3$, the cut is halved to 0.25-0.30 $\mu\text{g}/\text{m}^3$ for the Gradkos, the ALPHAs perform even better with an offset of only 0.1 $\mu\text{g}/\text{m}^3$. If the two extreme values at Zegveld are not taken into consideration, the offset at 0-5 $\mu\text{g}/\text{m}^3$ for both ALPHA samplers and Gradko samplers is 0.1 $\mu\text{g}/\text{m}^3$. This indicates that both methods show no significant deviation from the AMOR measurements close to $0 \mu\text{g}/\text{m}^3$.

With an even smaller measuring range of 0-3 $\mu\text{g}/\text{m}^3$, which in principle could provide the best information on the measurement performance close to $0 \mu\text{g}/\text{m}^3$, the slope and the offset can no longer be determined in detail, because due to noise, the data collection has the character of a point cloud. The explained variance of the regression line, which is always about 0.90 or higher for the different measuring ranges for both sampler types, falls back to 0.82 for the ALPHA samplers and 0.67 for the Gradko samplers in the range of 0-3 $\mu\text{g}/\text{m}^3$.

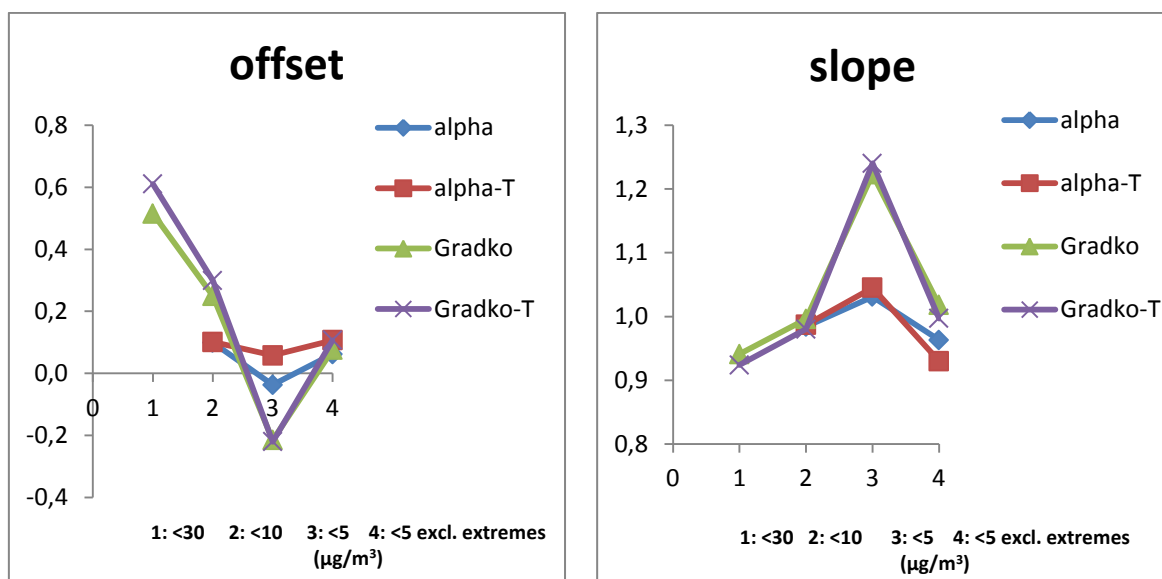


Figure B4.1: The offset of the Y axis and the slope for Gradko and ALPHA samplers with respect to AMOR measurements, both on the basis of individual sampler values and for the triplicate average (T), for the measurement paths 0-30, 0-10 and 0-5 $\mu\text{g}/\text{m}^3$, the range 0-5 $\mu\text{g}/\text{m}^3$ with and without the two strongly deviating triplicate average values at measurement location Zegveld.

Appendix 5: Background information on the comparison of DELTA denuders, Gradko and ALPHA samplers with AMOR data from Zegveld

A direct comparison of the monthly values of the DELTA denuders and the ALPHA samplers in Zegveld with the Gradko tubes is not possible. This is because the ALPHA samplers and the DELTA Denuders are exchanged every four weeks, usually on a Thursday, in contrast to the Gradko tubes that are exchanged every month around the 28th. To compare the measurements, the hourly ammonia values of the AMOR (NH_3 – AMOR) are taken as the basis and averages are calculated over three interval periods.

1. **Yellow**: a normal monthly average from the first to the last day of the month as standard is done in Anaconda,
2. **Blue**: an average over the time period of the instruments of CEH $\approx$ 4 weekly period,
3. **Red**: an average over the time period of the MAN $\approx$ monthly around the 28th of the month.

On the basis of these three averages, a factor was calculated to correct the ammonia concentration of the DELTA denuders, ALPHA Samplers and Gradko tubes to a normal monthly average.

The factors f_{CEH} and f_{MAN} are defined as follows:

$$f_{\text{CEH}} = \frac{\{\text{NH}_3 - \text{AMOR}\}^{\text{time period CEH}}}{\{\text{NH}_3 - \text{AMOR}\}^{\text{month}}}$$

$$f_{\text{MAN}} = \frac{\{\text{NH}_3 - \text{AMOR}\}^{\text{time period MAN}}}{\{\text{NH}_3 - \text{AMOR}\}^{\text{month}}}$$

The corrected monthly averages for the different instruments were calculated as follows:

$$\{\text{NH}_3 - \text{DELTA}\}^{\text{month}} = \frac{\{\text{NH}_3 - \text{DELTA}\}^{\text{time period CEH}}}{f_{\text{CEH}}}$$

$$\{\text{NH}_3 - \text{ALPHA}\}^{\text{month}} = \frac{\{\text{NH}_3 - \text{ALPHA}\}^{\text{time period CEH}}}{f_{\text{CEH}}}$$

$$\{\text{NH}_3 - \text{Gradko}\}^{\text{month}} = \frac{\{\text{NH}_3 - \text{Gradko}\}^{\text{time period MAN}}}{f_{\text{MAN}}}$$

Two methods were used to compare annual averages.

Method 1

The annual averages are calculated from 1 January to 31 December. The exposure duration is determined per measurement. This is to overcome two problems:

1. The measurements were not taken exactly every 4 weeks (CEH) or on the 28th (MAN).
2. With both instruments, the switch was not directly at the end of the year/ start of the new year. In order to calculate an annual average, the measured number of hours in December and in January were checked. Using this weighting, the December-January measurement was divided over the two years.

Expressed in formula:

$$\{\text{NH}_3\}^{\text{year}} = \sum \frac{\text{hr}_{\text{time period}} \cdot \{\text{NH}_3\}^{\text{time period}}}{\text{hr year}}$$

Method 2

Another method is to sum the measurements and then divide them by the number of measurements (n) taken in that year:

$$\{\text{NH}_3\}^{\text{year}} = \sum \frac{\{\text{NH}_3\}^{\text{time period}}}{n}$$

The results of the two methods for determining the annual average differ very little (Figure B5.1); the Gradko is almost on the 1: 1 line. The fact that the Gradko shows less shift than the DELTA is probably due to the fact that it has a time period of a month where the cut is always around the same time (~ 3 days in December, ~ 28 days in January). The CEH time period, thanks to the 4-week measurement, shows a greater shift in the number of days in December and January.

One reason for the small difference is that the concentration of ammonia in December and January is not very high; in the winter period, farmers are not allowed to apply manure. As a result, the precise distribution of the ammonia concentration in the December-January measurement does not play an important role.

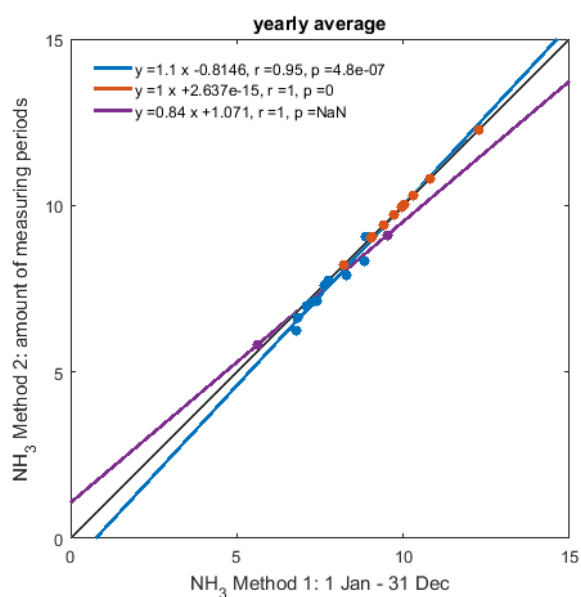


Figure B5.1: The yearly ammonia concentration calculated with the two methods for the three instruments: DELTA, Gradko, ALPHA. x-axis: from 1 January to 31 December, using the amount of hours per measurements, y-axis: sum of all measurements divided by the amount of measurements.

Regression for ADC converter:

DELTA: $y = 1.1x - 0.8146, r = 0.95, p = 4.8 \cdot 10^{-7}$

Gradko : $y = 1x - 5.169 \cdot 10^{-15}, r = 1, p = 2.5 \cdot 10^{-117}$

ALPHA : $y = 0.84x + 1.071, r = 1$

Appendix 6: Comparison with COTAG measurements

The Gradko samplers can also be compared with the COTAG measurements (Stolk et al. 2014). The COTAG measurements at a height of 0.8 meters are performed during three categories of meteorological conditions. By combining the measurements from these three categories, the average ammonia concentration of the month in question is derived at a height of 0.8 meters. This can be compared with the monthly average values of the Gradko samplers.

There are series available for the COTAG and Gradko at three locations that can be compared. These are usually triplicate Gradko samplers that were attached to the COTAG itself at the same height as the COTAG measurement. However, the three Gradko samplers in De Veenkampen were present at three different locations at a distance of 150 to 250 meters from the COTAG, with a mutual distance of 150 to 330 meters. From April 2012 to June 2014 in Bargerveen, Gradko samplers were employed that were not used in the MAN due to circumstances. Part of these samplers has been stored unused for a few months prior to their use, making these measurements less reliable.

Table B1 Measurement series on the COTAG sites

Location	Period	Remarks	Height Gradko (m)	Height COTAG (m)
Bargerveen	Apr 2012 - Jun 2014	Partially old samplers	0.8	0.8
Bargerveen	Jul 2014 - Aug 2015		0.8	0.8
Oostelijke Vechtplassen	Jul 2014 - Aug 2015		0.8	0.8
De Veenkampen	Sep 2012 - Jan 2014	Large distance COTAG	1.8	0.7

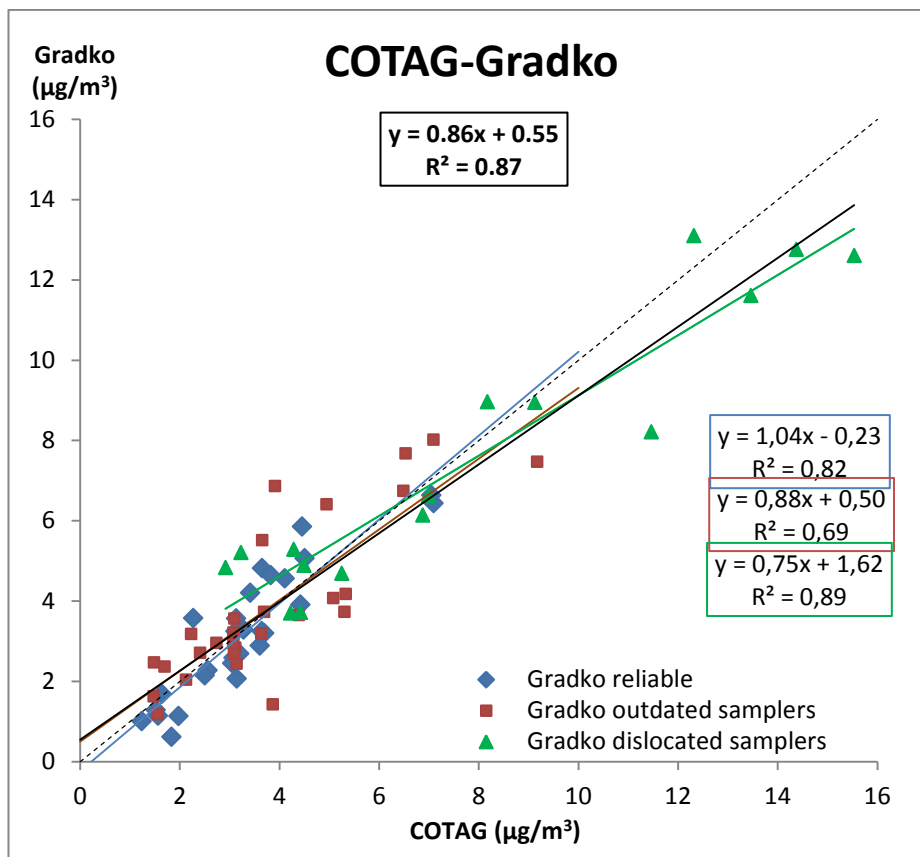


Figure B6.1: comparison of Gradko measurements with COTAG measurements.

There is a fairly good agreement between both measurement techniques (Figure B6.1). The series with 33 "reliable" Gradko measurements scores best with an explained variance of 82% and an offset of $-0.2 \mu\text{g}/\text{m}^3$. The series with 31 observations with partially outdated Gradko samplers from Bargerveen has an explained variance of 69% and an offset of $0.5 \mu\text{g}/\text{m}^3$. The series with measurements at greater mutual distance from the Veenkampen has a large offset of $1.6 \mu\text{g}/\text{m}^3$, but has an explained variance of 89%. Together they exhibit an explained variance of 87% and offset of $0.6 \mu\text{g}/\text{m}^3$. This offset is mainly caused by the measurements on the Veenkampen, probably due to the large mutual distance between the measurement locations there. The range that offers the most reliable equation has an offset of only $-0.2 \mu\text{g}/\text{m}^3$, so there is probably no significant offset.

The conclusion is that the Gradko sampler measurements correspond fairly well with those of the COTAG.

Appendix 7: The annual pattern in meteorological parameters

The meteorological data are from the Royal Netherlands Meteorological Institute (KNMI). For the analysis of MAN data, we use the monthly averages (from the 28th to the 28th) measured at the nearest KNMI station (Table B2).

Table B2 Nearest KNMI stations.

LML station		KNMI station
131	Vredepeel	375 Volkel
444	De Zilk	210 Valkenburg 240 Schiphol in 2016
538	Wieringermeer	249 Berkhout 235 De Kooy in 2015 and 2016
633	Zegveld	240 Schiphol
738	Wekerom	275 Deelen
929	Valthermond	279 Hoogeveen

Figure B7.1 shows the monthly averages of the meteorological parameters Temperature (T), Radiation (Q), Pressure (P), Rain quantity (DQ), Rain duration (DT), Relative humidity (RH), Wind direction (WD) and wind speed (WV).

There is a clear annual pattern in T and Q with a minimum in winter and maximum in summer. P is relatively constant during the year, but has more spread in the winter months. RH has a clear minimum in the summer. Furthermore, we see that the precipitation duration (DT) is longer and the wind speed is higher during the winter, and that an easterly wind occurred only in the spring.

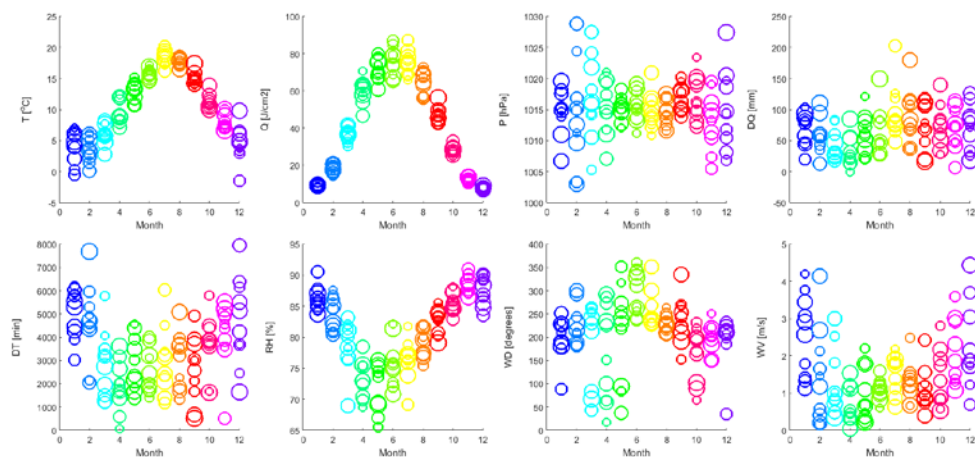


Figure B7.1 The meteorological parameters measured at the KNMI-station the Bilt for the different months. The size of the circle indicate the measurement year, the smallest circle is 2005 and the largest circle 2016.

Appendix 8: Seasonal trend in the distribution within triplicate measurements

From September 2011, at least at one location triplicate measurements takes place in all nature reserves. Figure B8.1 shows box plots and the average of the standard deviation of the calibrated triplicate measurements against time (left) and against measurement month (right). The blue box indicates the 25 and 75 percentile, the red line in the box is the median. The red pluses are outliers. The upper graphs show the absolute standard deviation and the lower the relative ones.

In 2012, the standard deviation in the triplicate average appears to have an increase with a maximum in summer. But in the years thereafter this cannot be seen; a peak occurs in the spring months. Looking at all the years together (right figures), there is no clear seasonal cycle. The peak in the absolute standard deviation in the triplicate mean in the spring can be caused by the higher values in ammonia concentration; in that situation the absolute measurement inaccuracy is greatest. The lower figures therefore show the relative standard deviation in the triplicate average. The relative standard deviation has the highest values in the winter months when the concentrations are low and the relative measurement inaccuracy in the measurement is greatest.

The pattern found in the spread in triplicate measurements thus appears to be explained by the known absolute and relative measurement inaccuracy (Lolkema *et al.* 2015). No influences of meteorology can be determined.

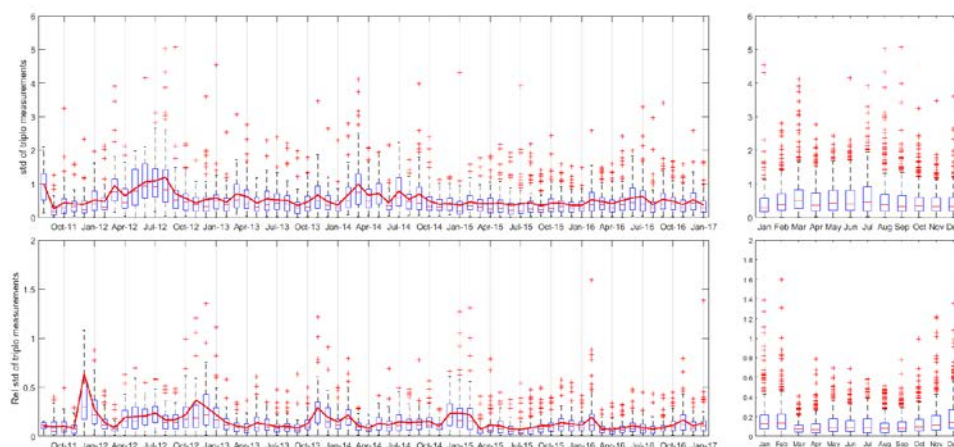


Figure B8.1 Boxplots and the average of the standard deviation (above) and relative standard deviation (below) of the triplicate-measurements from September 2011 against time (left) and against measuring month.

Appendix 9: Meteorological influences on not calibrated Gradko measurements

Preface

This appendix discusses the extent to which the performance of the Gradko samplers in the MAN measurement network depends on meteorological conditions.

Gradko tubes are passive samplers. This means that the ammonia concentration is determined by the principle of molecular diffusion. It is known that temperature and pressure influence molecular diffusion. The diffusion coefficient with which Gradko determines the ammonia concentration is a fixed value, while during the year the monthly average temperature and pressure vary. This affects the measured values of the samplers. To correct this together with other disruptive conditions, the values of the Gradko samplers are calibrated each month with AMOR measurements from the LML stations (5 or 6 stations).

Because the monthly average temperature show a yearly trend, we also look at the influence of meteorology on whether the measured value depends on the measurement month. We investigate whether the following parameters are sensitive to meteorological conditions or the month when measured:

1. variation in the triplicate measurements
2. ratio $\frac{NH_{3LML}}{NH_{3MAN}}$ (used in the calibration)
3. the calibration constant of the linear regression
4. ratio $\frac{NH_{3LML}}{NH_{3MAN}}$ after correction
5. the total correction factor for ammonia concentrations at 1, 5, 10 and 15 $\mu g/m^3$.

This appendix is therefore an extension to section 3.1 by Lolkema *et al.* 2015, where the focus is on the calibration constants and a temperature dependency and where only data is analysed up to and including 2012.

Data

From September 2011, triplicate measurements were carried out at one location per nature reserve. For the calibration of the Gradko samplers, we used measurements at 5 (up to and including December 2008) and 6 (as of January 2009) LML stations. These measurements on LML stations were carried out as triplicates from the beginning. The (triplicate average) ammonia concentration measurements of the Gradko samplers ($NH_3 MAN$) are calibrated with the ammonia concentration measured at the LML stations ($NH_3 LML$). Up to and including October 2015, measurements were taken at the LML locations with the AMOR, and from November 2015 with the mini-DOAS. The ammonia concentration measured with the AMOR has been increased by a small offset caused by an inverter that converts the digital AMOR signal into an analogue signal (Digital-to-Analogue Converter; DAC). In general, the offset caused by DAC is stable per system, but it varies per station.

In 2016 there were several problems with the mini-DOAS; these data were corrected afterwards. The data presented here contain a provisional correction, which will be improved in the course of 2018.

The calibration of the Gradko samplers has a linear regression on the triplicate means of the ammonia concentration measured with the Gradko samplers at the LML stations with the ratio between LML and MAN (Lolkema *et al.* 2015 section 3.1):

$$\frac{\text{NH}_3_{\text{LML}}}{\text{NH}_3_{\text{MAN}}} = a + b \cdot \text{NH}_3_{\text{MAN}}$$

The calibration constants, a and b , are not constant; they are determined every month. Lolkema *et al.* 2015 show, due to start-up problems, that the calibration constants fluctuate more in the first two years, so we started the analysis from January 2007 onwards.

For the analysis of the ratio between the LML and MAN we used the average ammonia concentration values over the exposure duration of the Gradko samplers. The data from the nearest KNMI station were used for meteorological input (Appendix 7). Due to the availability of data from certain stations, differences may occur per year.

Results

The illustrations B9.1 to B9.6 show the proposed ratio $\frac{\text{NH}_3_{\text{LML}}}{\text{NH}_3_{\text{MAN}}}$ for the six different stations for the whole period, for a year, and against the meteorological parameters (nearest KNMI station). For the wind direction, we show a compass rose instead of a linear correlation. The white line in the rose shows the average ratio per 30° wind sector. The allocation to a certain wind sector is based on the monthly average wind direction. The red line is the weighted rose, it has been corrected to account for the fact that some wind directions (especially from 180° - 270°) occur more often. If the ratio was evenly distributed, although there is a preferred wind direction, then the red line would be a perfect circle.

We see that for the low-concentration stations (444 De Zilk, 929 Valthermond), the ratio fluctuates more than for the high-concentration stations where it is more consistently around one (131 Vredepeel and 738 Wekerom).

It appears that the r^2 (determination coefficient, for a linear regression equal to the squared correlation coefficient) is low for all meteorological parameters. In general, per station, the highest correlations with the ammonia ratio are for temperature, radiation and relative humidity. The p-value of the linear regression for T , Q and RH is less than 0.05. The p-values are higher for the stations with low ammonia concentrations than for the stations with high concentrations.

The correlation of the ratio with T and Q is positive, while the correlation with RH is negative. This is due to the strong correlation of T and Q and anti-correlation with RH . For all stations, a temperature of about 20 °C has a ratio of 1. This is probably due to the fact that the concentrations at these stations are corrected to standard pressure and a standard temperature of 20 °C.

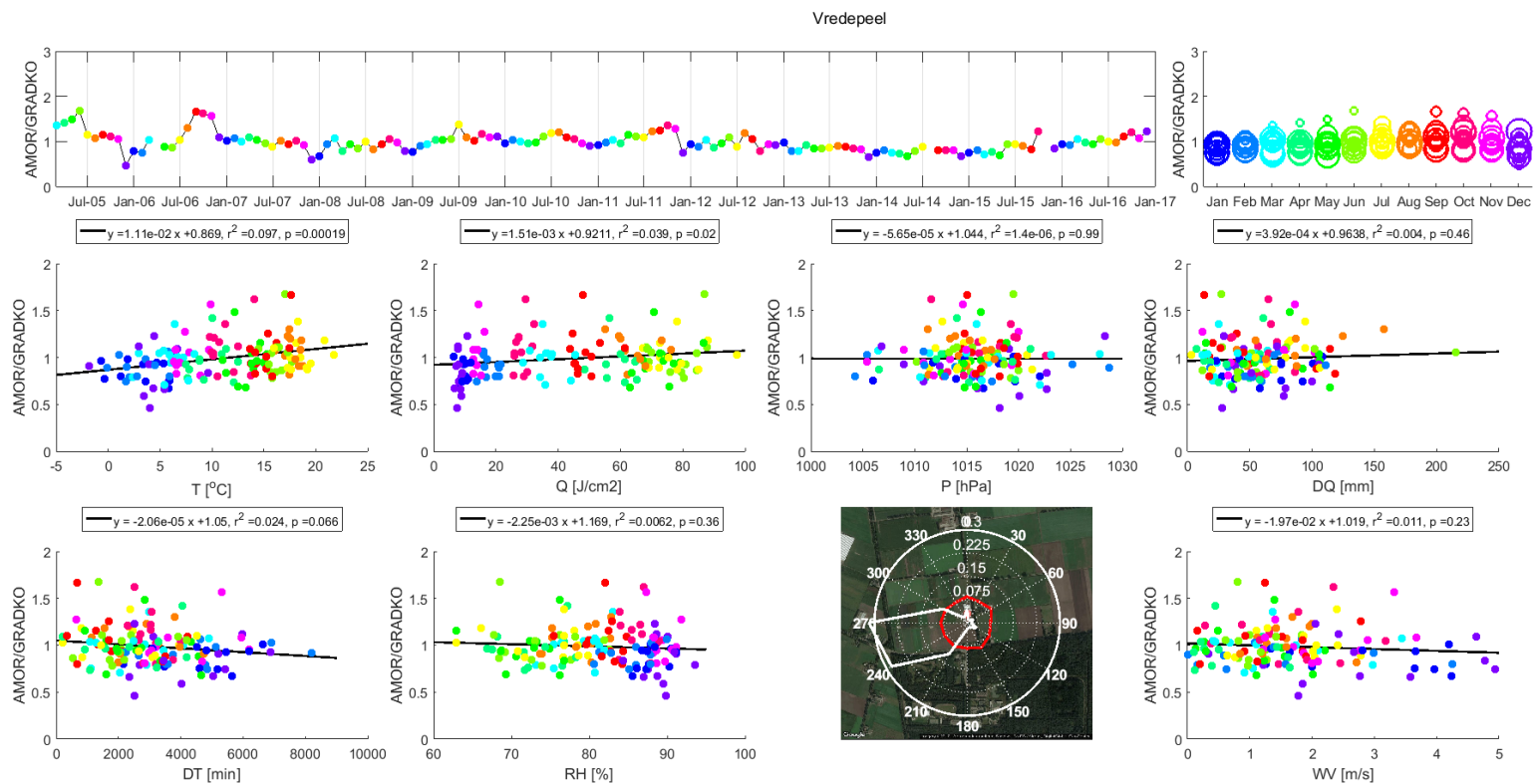


Figure B9.1 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 measured at Vredepeel.

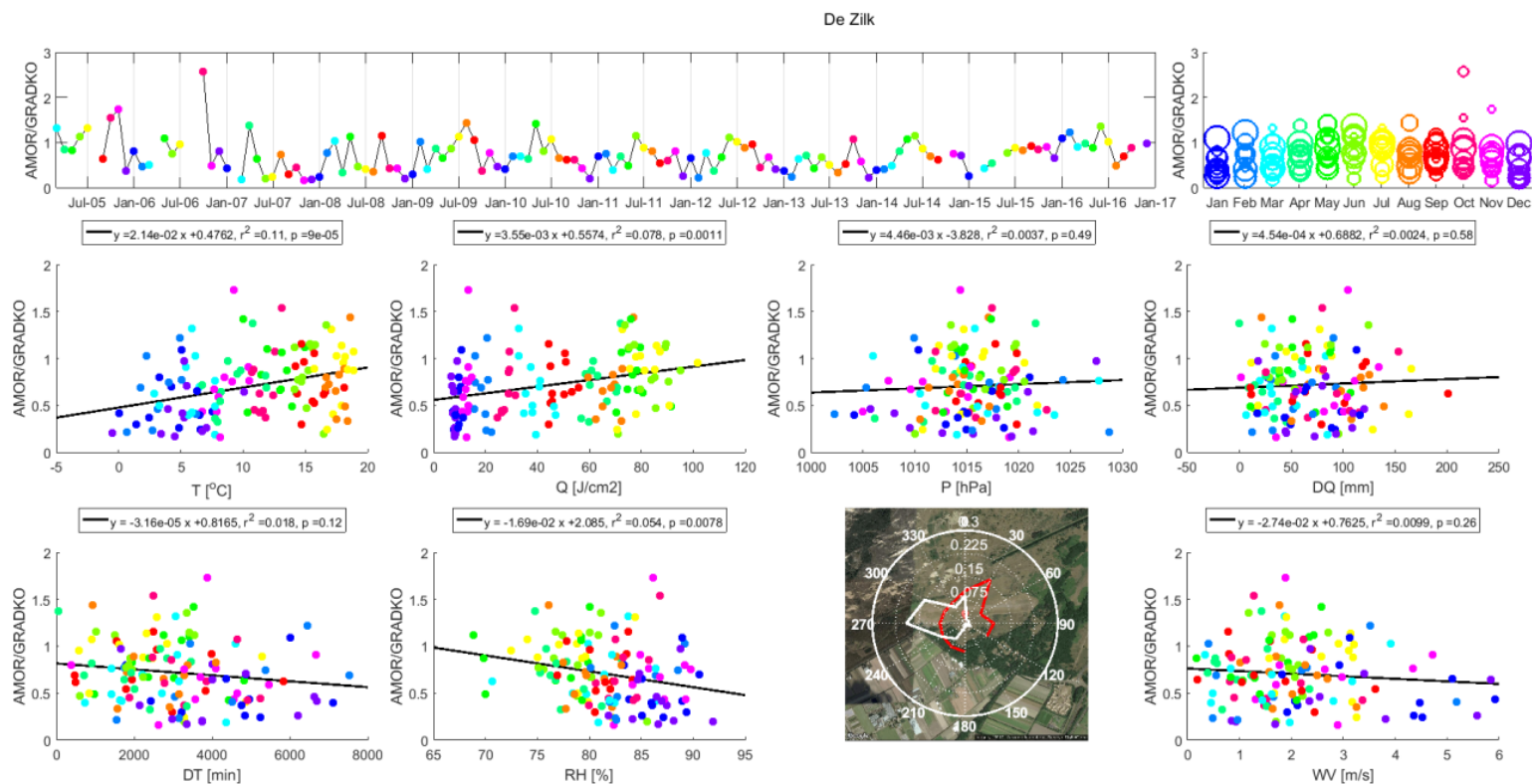


Figure B9.2 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 measured at De Zilk.

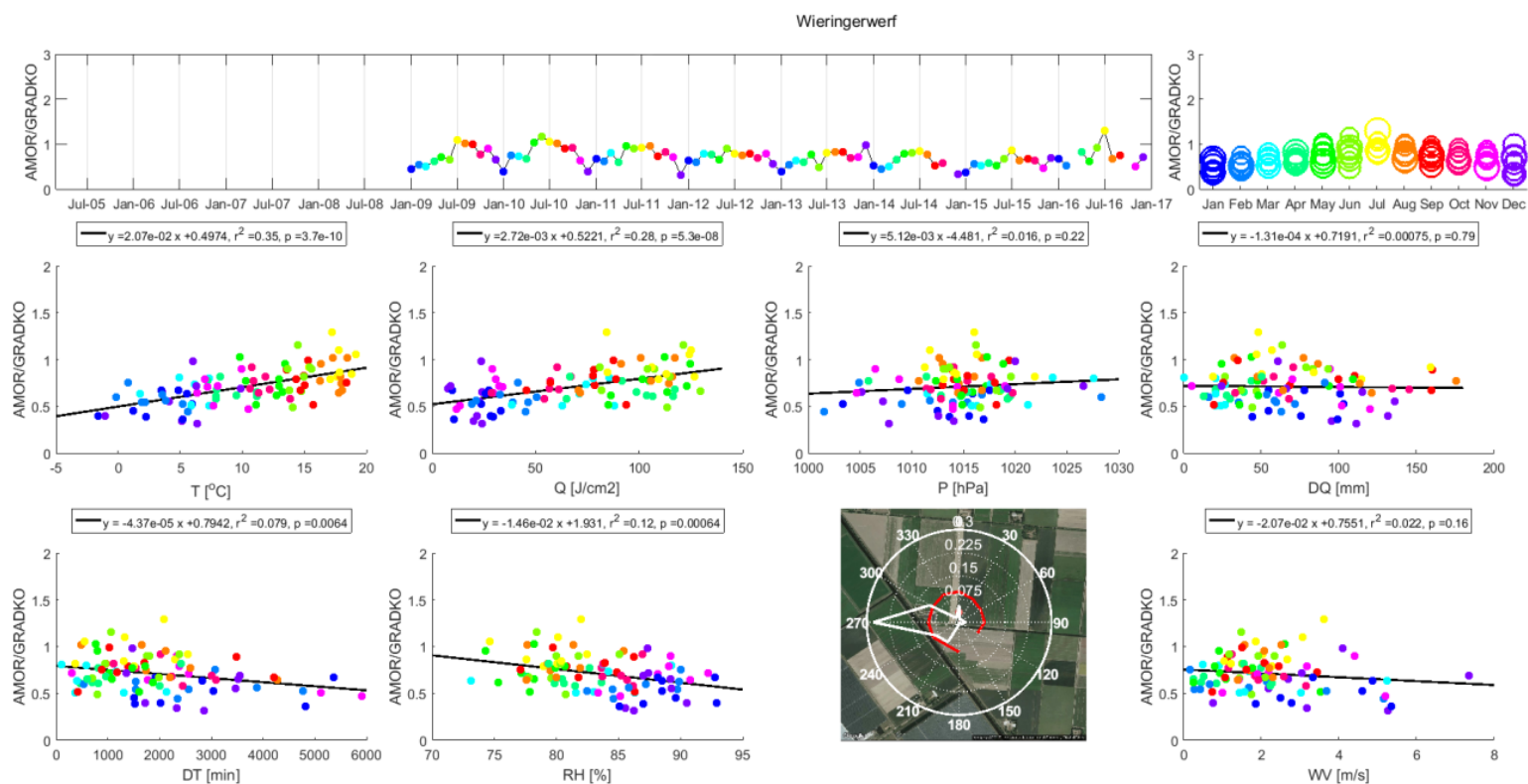


Figure B9.3 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 measured at Wieringerwerf.

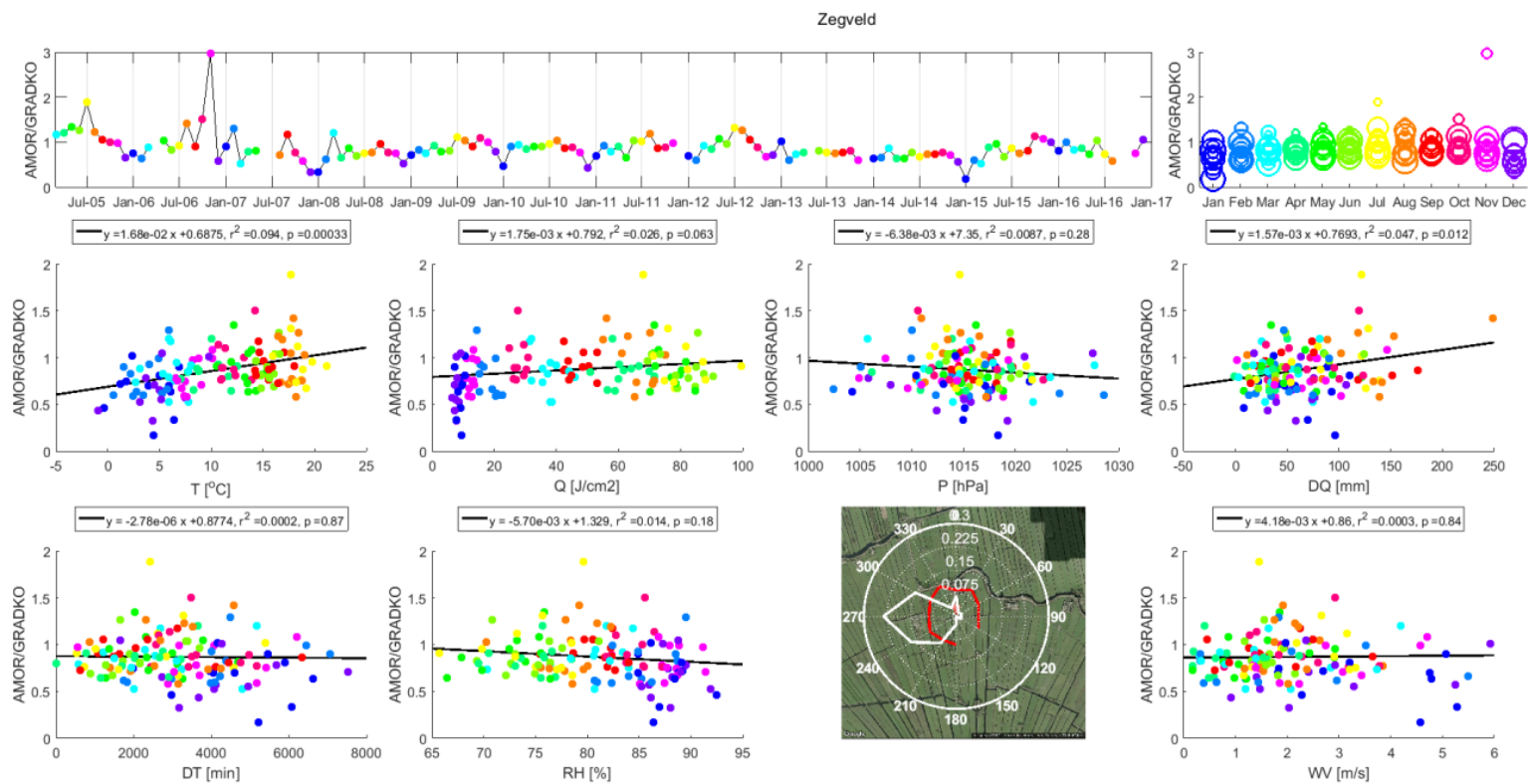


Figure B9.4 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 measured at Zegveld.

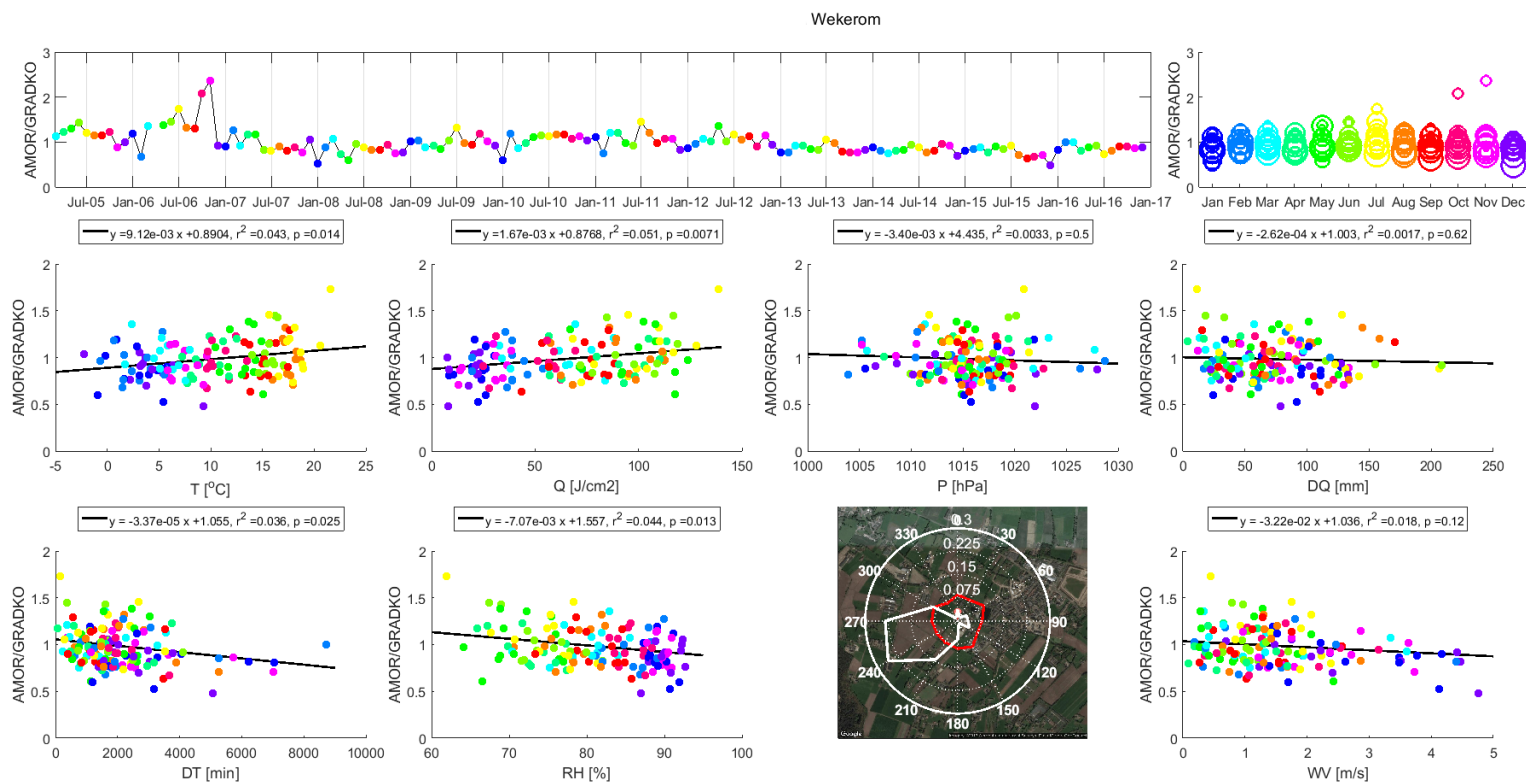


Figure B9.5 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 measured at Wekerom.

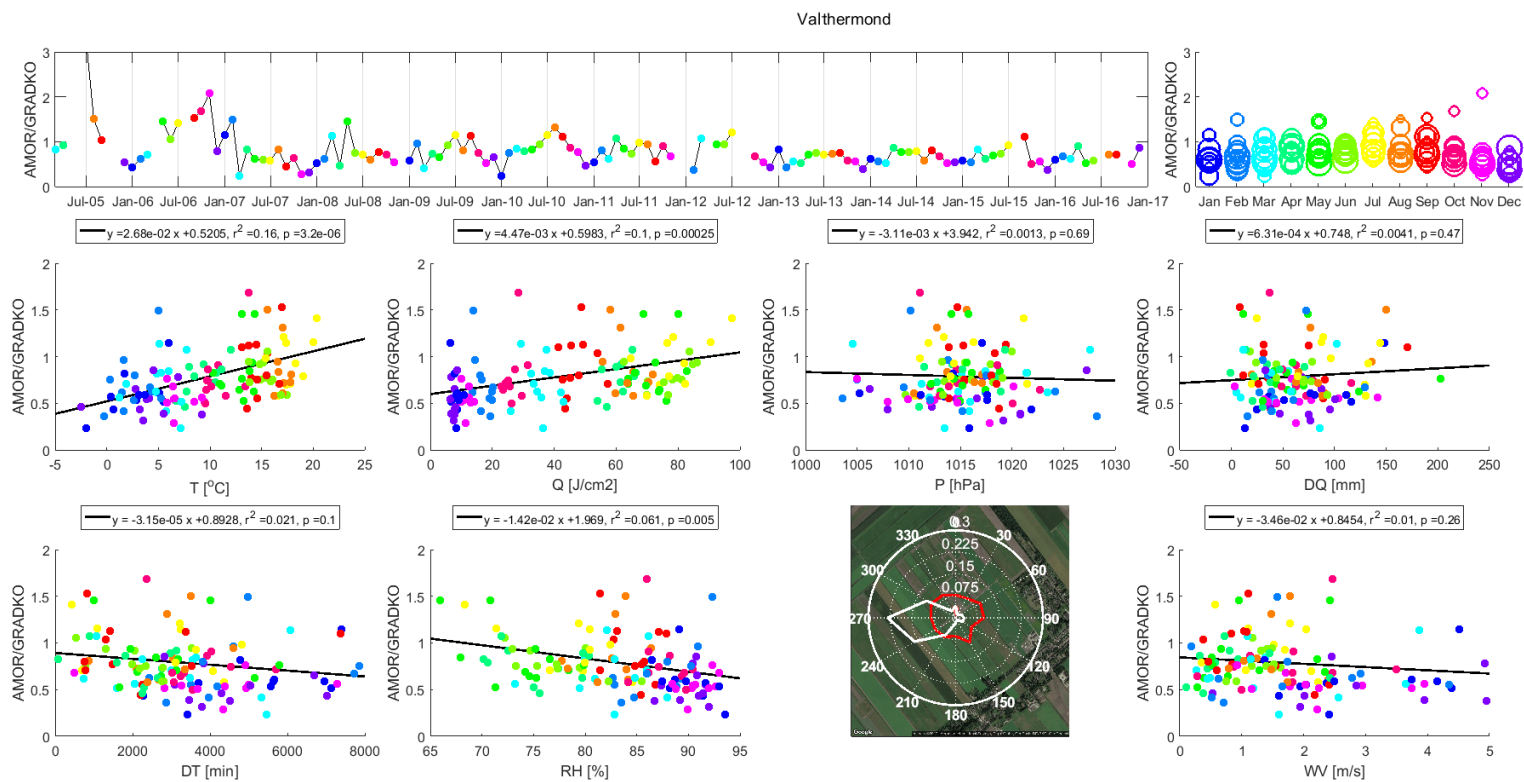


Figure B9.6 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 measured at Valthermond.

In addition, the statistical relationship between the ratio and all meteorological parameters together was investigated. Input is the ratio and normalized meteorological parameters, whereby the values of the coefficients a_1 to a_8 can be compared.

$$\frac{NH_{3_LML}}{NH_{3_MAN}} = \text{intercept} + a_1 \cdot \frac{T}{T} + a_2 \cdot \frac{Q}{Q} + \dots + a_8 \cdot \frac{WV}{WV}$$

The model automatically determines which terms should be included statistically. Because we are only interested in a connection of the meteorological parameters underlying a physical interpretation, we only looked at the linear terms and not at cross-combinations (TQ etc.). If the AMOR measurements and the GRADKO measurements are always equal to each other and do not depend on meteorological parameters, then only the intercept would remain and would have the value one. If the influence of a meteorological parameter is more important, the value of the a_x coefficient of this parameter will be higher. The model also gives the t-stat value of these coefficients, only when t-stat is greater than 2 is the term statistically significant. The first column of Table B3 shows the results of the linear regression, the colour indicates a range of t-stat. The temperature is the most important for most stations. For the stations with high ammonia concentrations, we see that the value of the intercept is closer to one (Estimate) and the value of T is smaller, while the stations with lower concentrations have a lower value for the intercept and a higher value for meteorological parameters.

Table B3 The values of the a coefficient included in the statistical model. In red, the absolute values of t-stat are less than 2 and in orange less than 4. If t-stat is greater than 2, the term is statistically significant.

Station		Not calibrated	r^2	Calibrated	r^2
131	Vredepeel	$= 0.87 + 0.12 \frac{T}{T}$	0.09	$= -5.59 + 6.57 \frac{P}{P} - 0.03 \frac{WV}{WV}$	0.04
444	De Zilk	$= 0.48 + 0.23 \frac{T}{T}$	0.11	$= 0.98 + 0.06 \frac{Q}{Q} - 0.10 \frac{WD}{WD}$	0.02
538	Wieringer-meer	$= -0.35 + 0.18 \frac{T}{T} + 0.12 \frac{Q}{Q} + 0.76 \frac{RH}{RH}$	0.38	$= 0.25 + 0.09 \frac{DQ}{DQ} - 0.10 \cdot \frac{DT}{DT} + 0.71 \frac{RH}{RH}$	0.06
633	Zegveld	$= 0.69 + 0.18 \frac{T}{T}$	0.08	$= 0.63 + 0.37 \frac{RH}{RH}$	0.01
738	Wekerom	$= 0.96 + 0.08 \frac{T}{T} - 0.06 \frac{DT}{DT}$	0.05	$= 1.24 - 0.12 \cdot \frac{T}{T} - 0.05 \frac{DT}{DT}$	0.12
929	Valther-mond	$= 0.52 + 0.27 \frac{T}{T}$	0.15	$= 0.85 + 0.13 \cdot \frac{T}{T}$	0.09

Appendix 10: Meteorological influences on calibrated Gradko measurements

Appendix 9 shows that the ratio between AMOR-LML measurements and uncalibrated Gradko samplers is mainly temperature-dependent. To correct this, the Gradko samplers are calibrated monthly to the AMOR data. We therefore see a sensitivity to the temperature at the calibration constant a (Figure 14). This appendix describes the meteorological sensitivity of the calibrated Gradko values.

Figures B10.1 to B10.6 show that after the calibration, the ratio AMOR/Gradko fluctuates much less than before calibration (Appendix 9). The meteorological sensitivity is also strongly reduced. This can also be seen in the statistical model (see Table B3). First, for the r^2 , the calibrated data is smaller, which means that the correlation between the measured value and the model is smaller. Second, the t-stat of the a_x coefficient is often smaller than 2 or 4, which means that the included term is less statistically significant.

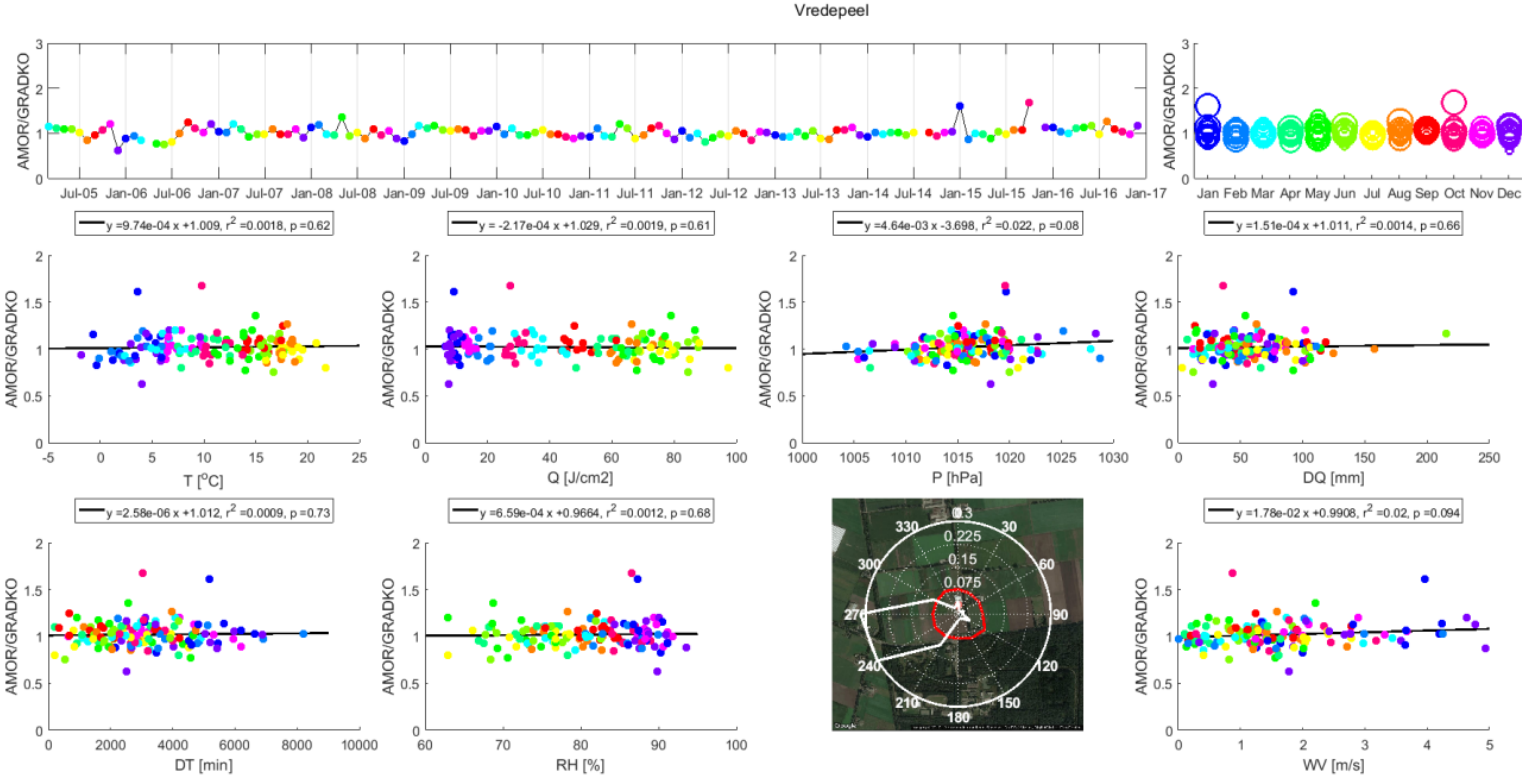
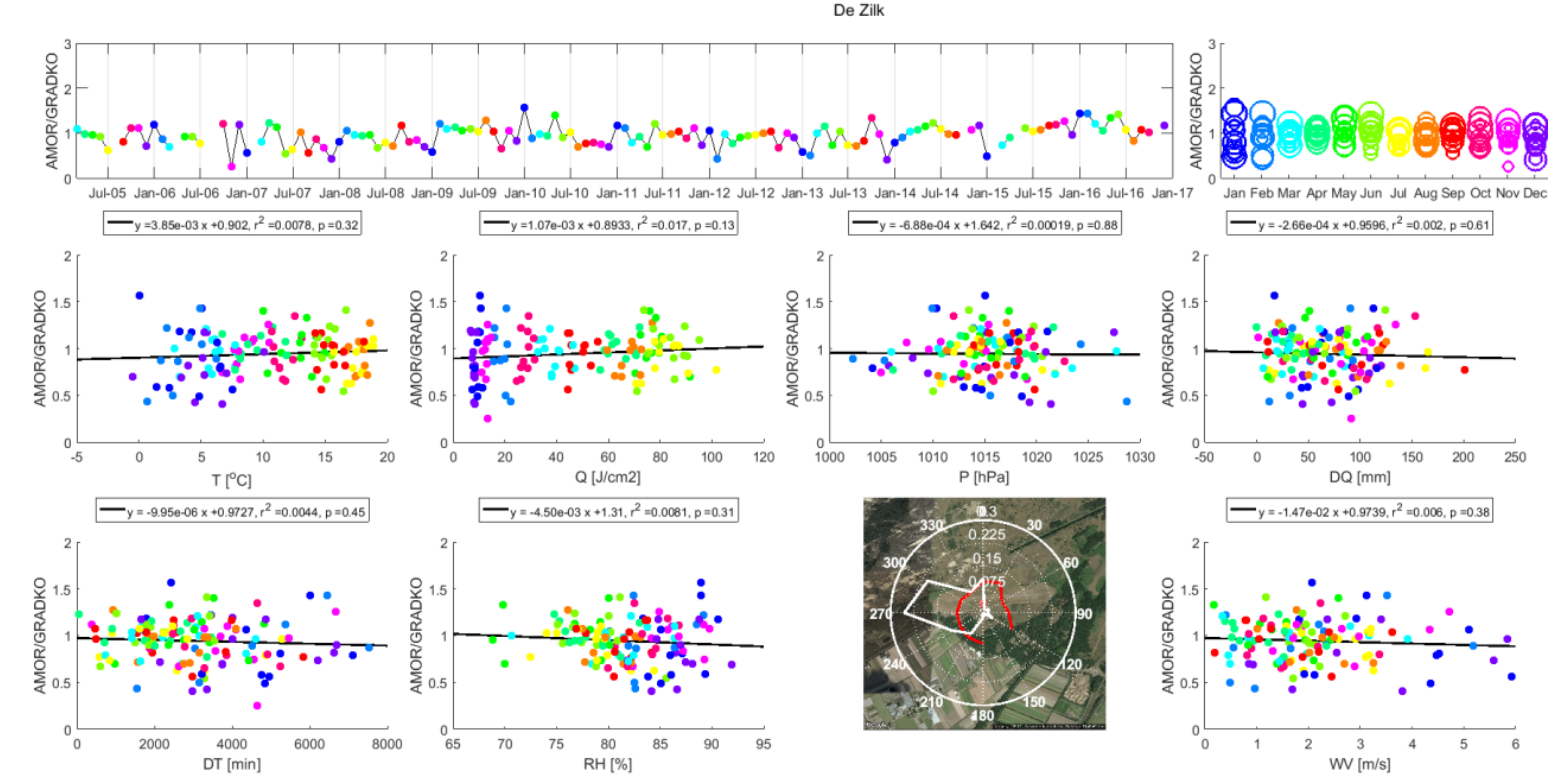


Figure B10.1 As in Figure B9.1 but now for the calibrated values



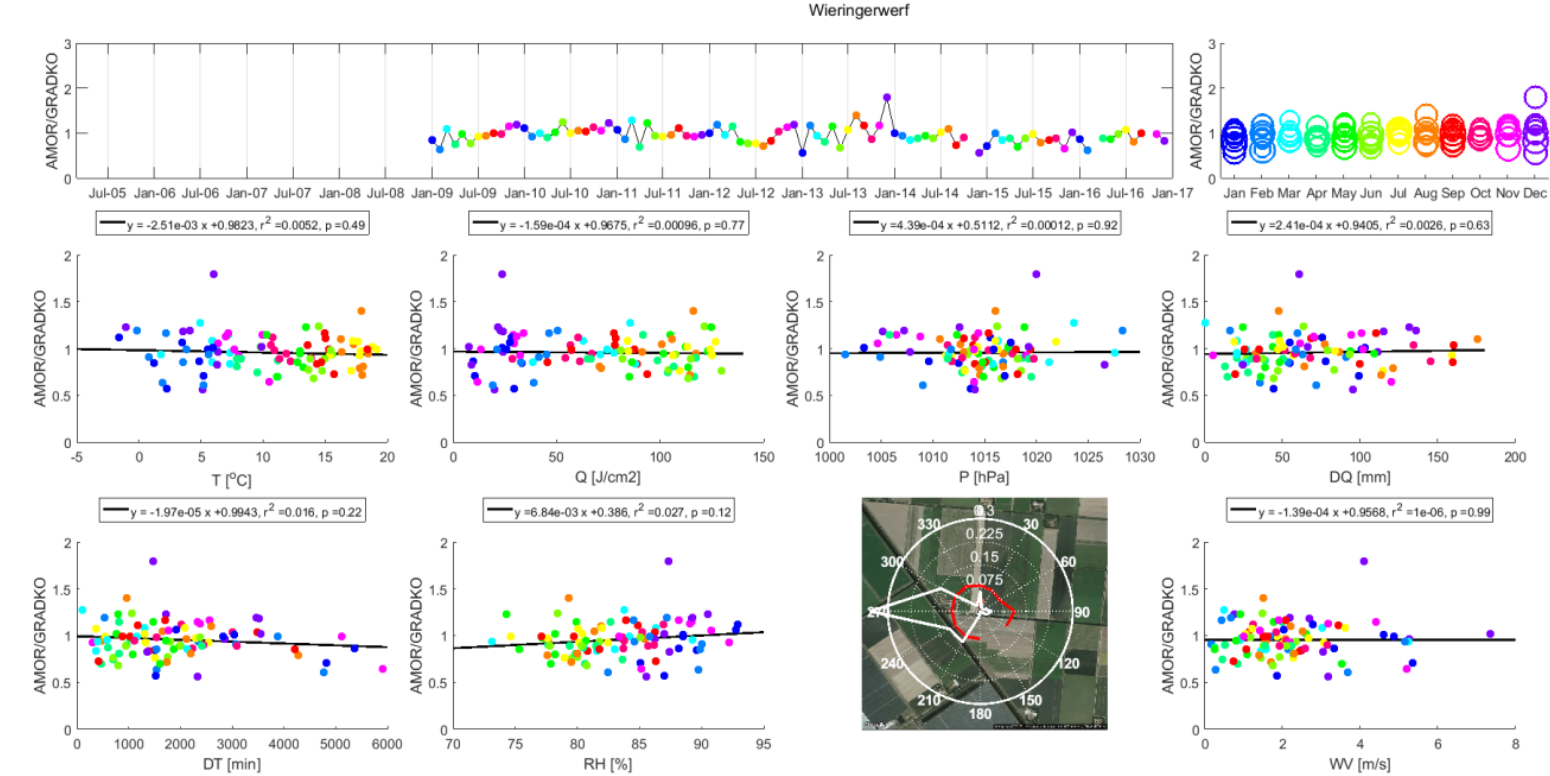


Figure B10.3 As in Figure B9.3 but now for the calibrated values

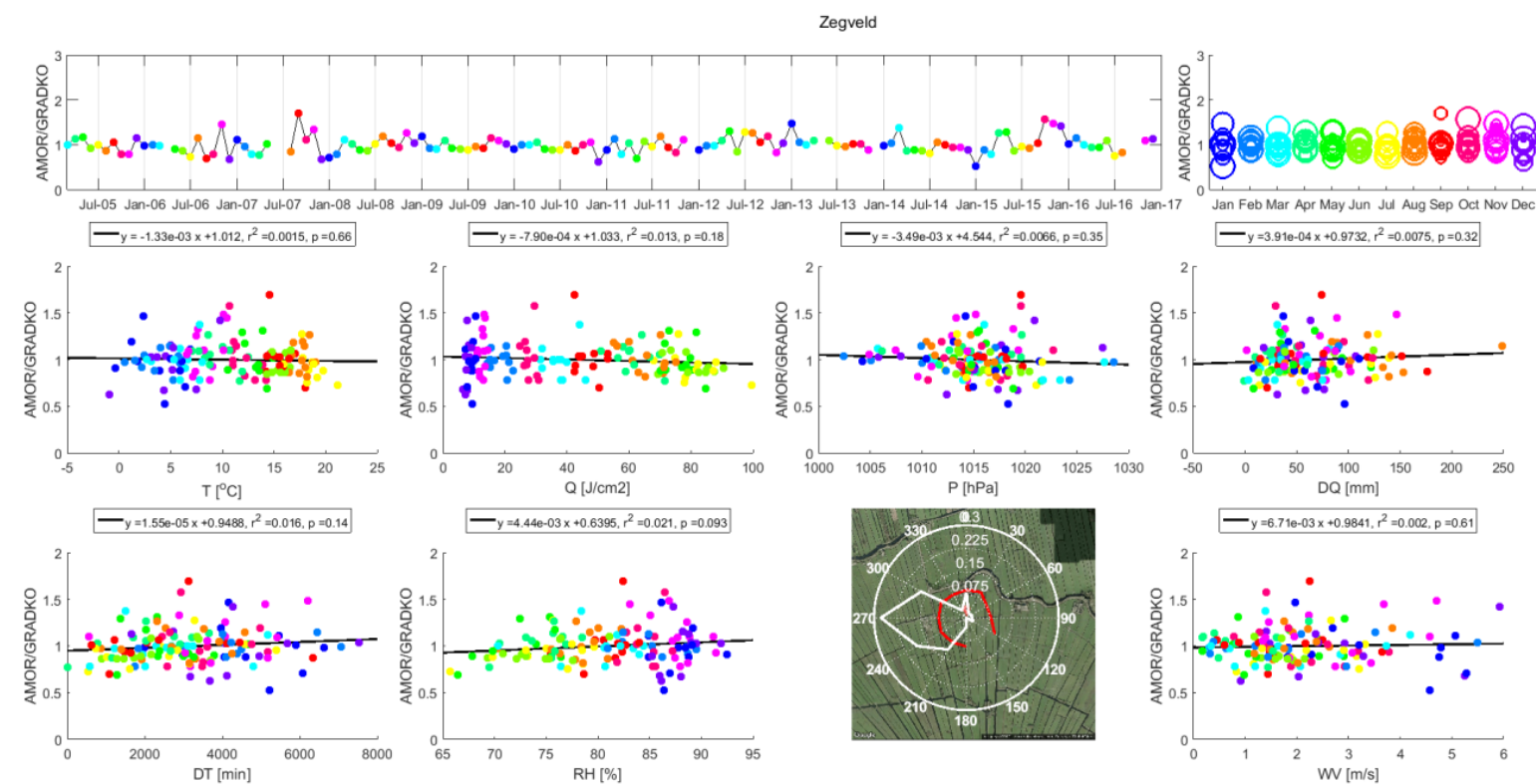


Figure B10.4 As in Figure B9.4 but now for the calibrated values

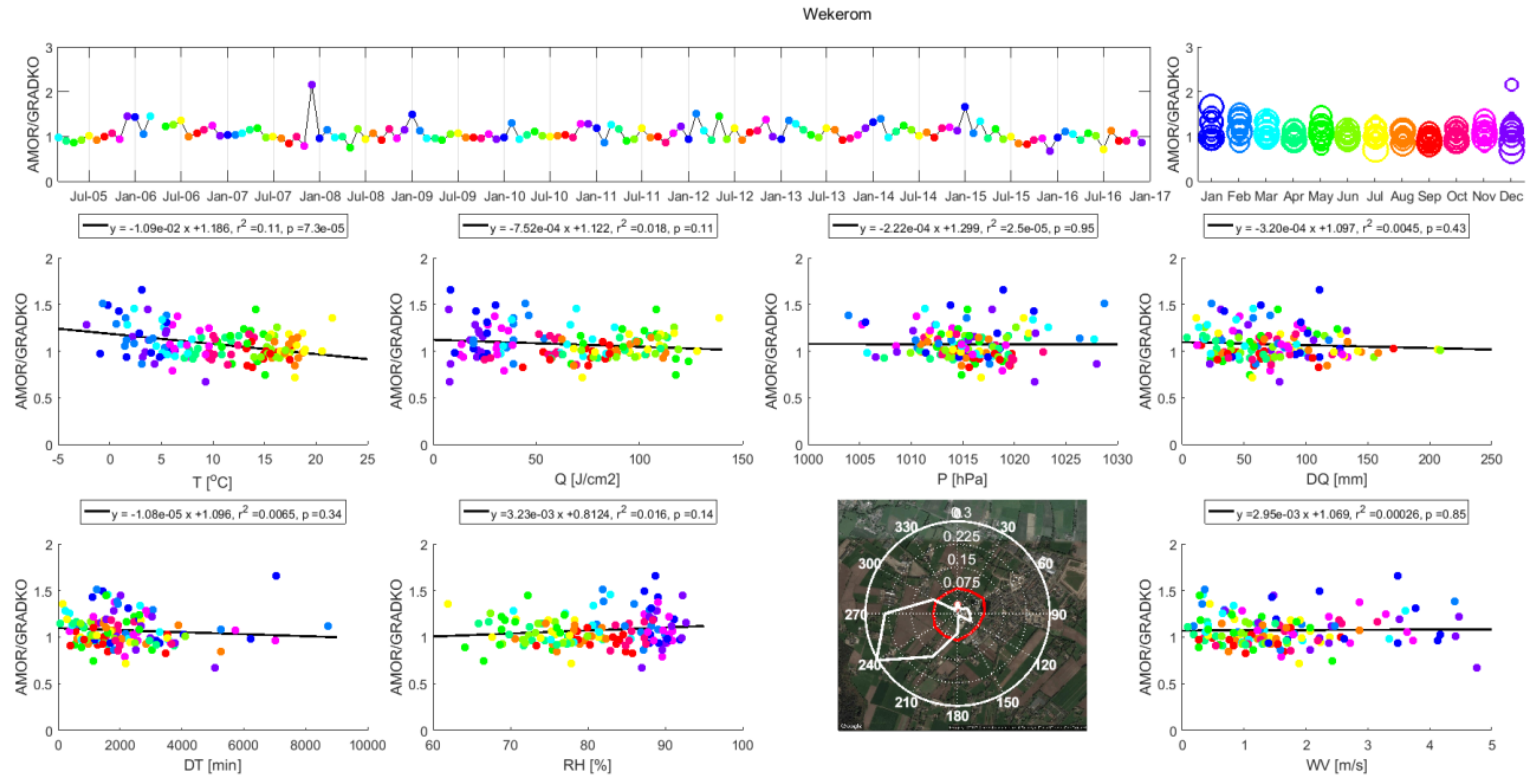


Figure B10.5 As in Figure B9.5 but now for the calibrated values

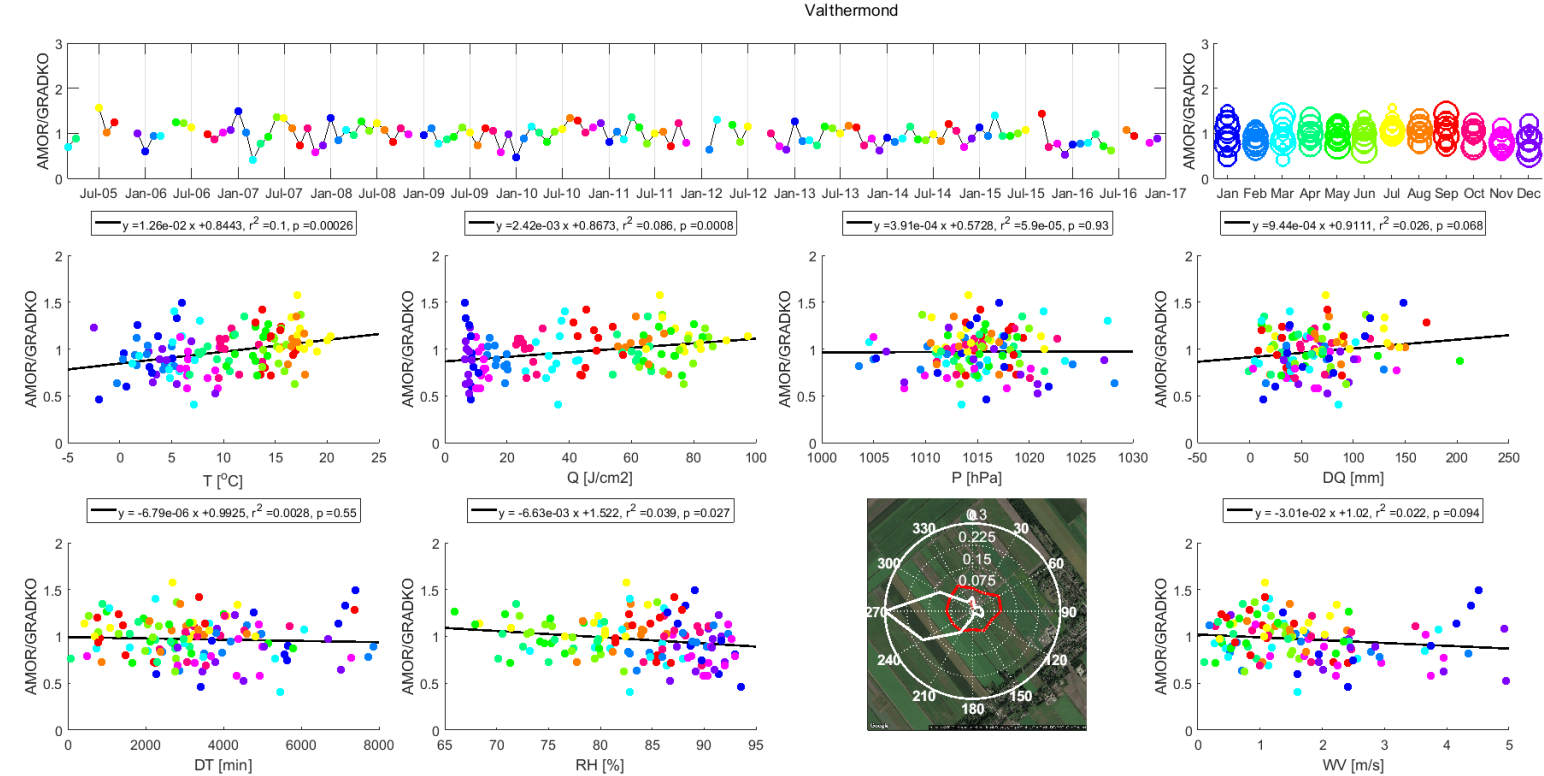


Figure B10.6 As in Figure B9.6 but now for the calibrated values

Appendix 11: Meteorological influences on uncalibrated Gradko measurements, depending on the concentration

The calibration function has an offset and a slope that both behave differently per measuring period, with the offset being maximal in summer and the maximum slope in winter. To investigate this further, the effective calibration factor and the meteorological influence on it have been determined for ammonia concentrations of 1, 5, 10, 15 and 20 $\mu\text{g}/\text{m}^3$.

Because the ratio between LML and uncalibrated Gradko measurements differs for stations with low and high ammonia concentrations, it can be expected that the influence of meteorology will be greater at low ammonia concentrations than for the higher values. This is confirmed in Figures B11.1 to B11.5.

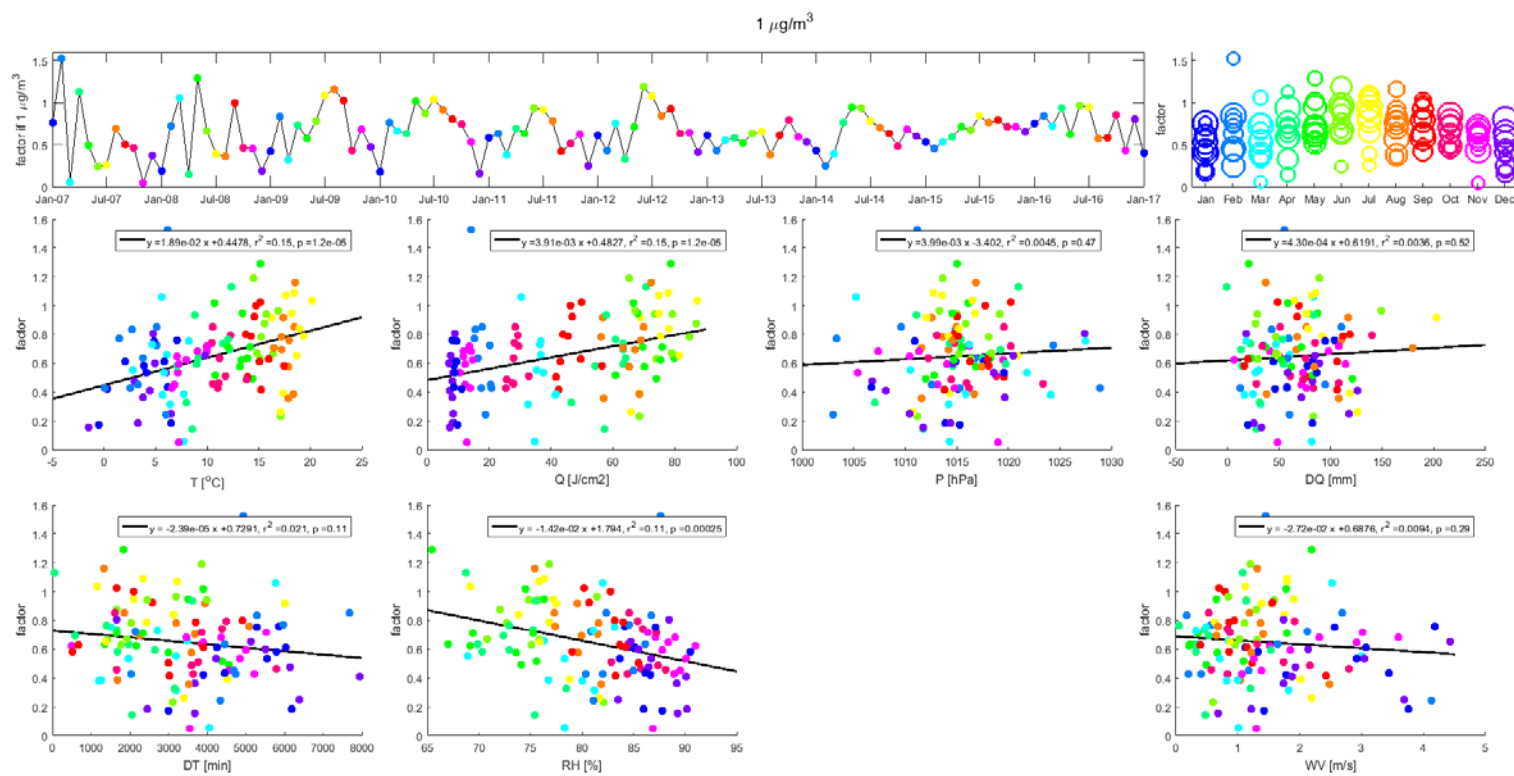


Figure B11.1 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 for a concentration level of about $1 \mu\text{g}/\text{m}^3$.

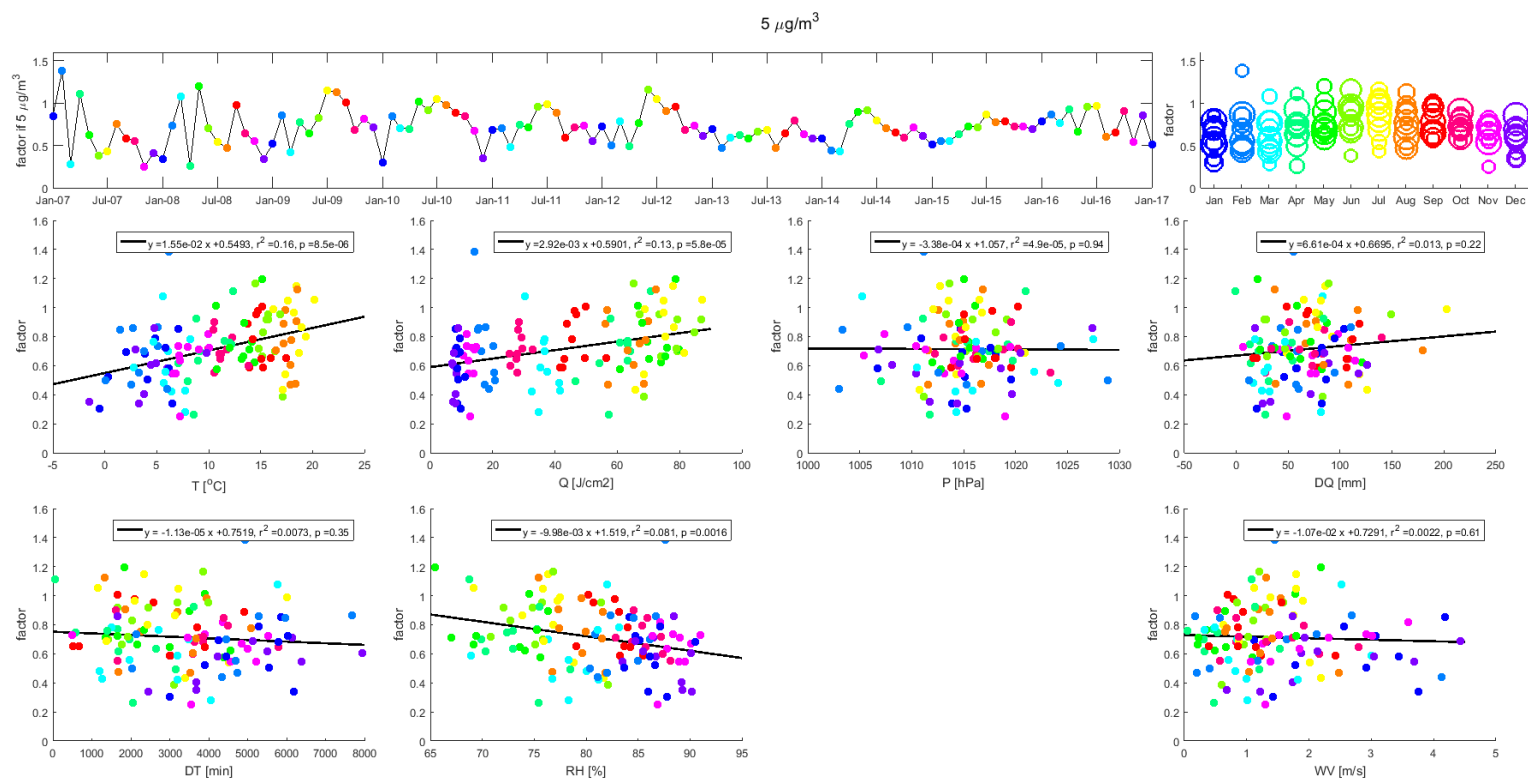


Figure B11.2 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 for a concentration level of about $5 \mu\text{g}/\text{m}^3$.

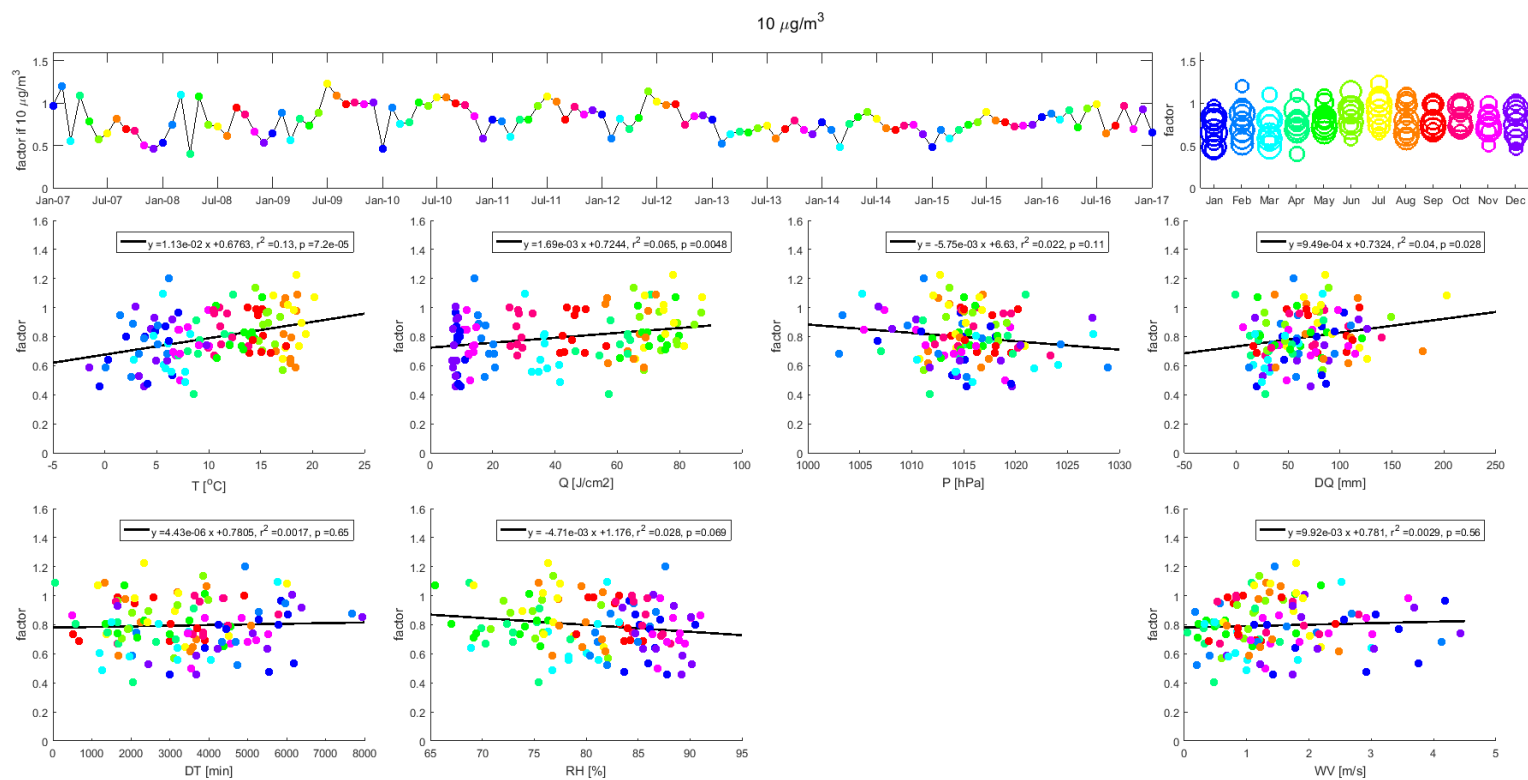


Figure B11.3 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 for a concentration level of about $10 \mu\text{g}/\text{m}^3$.

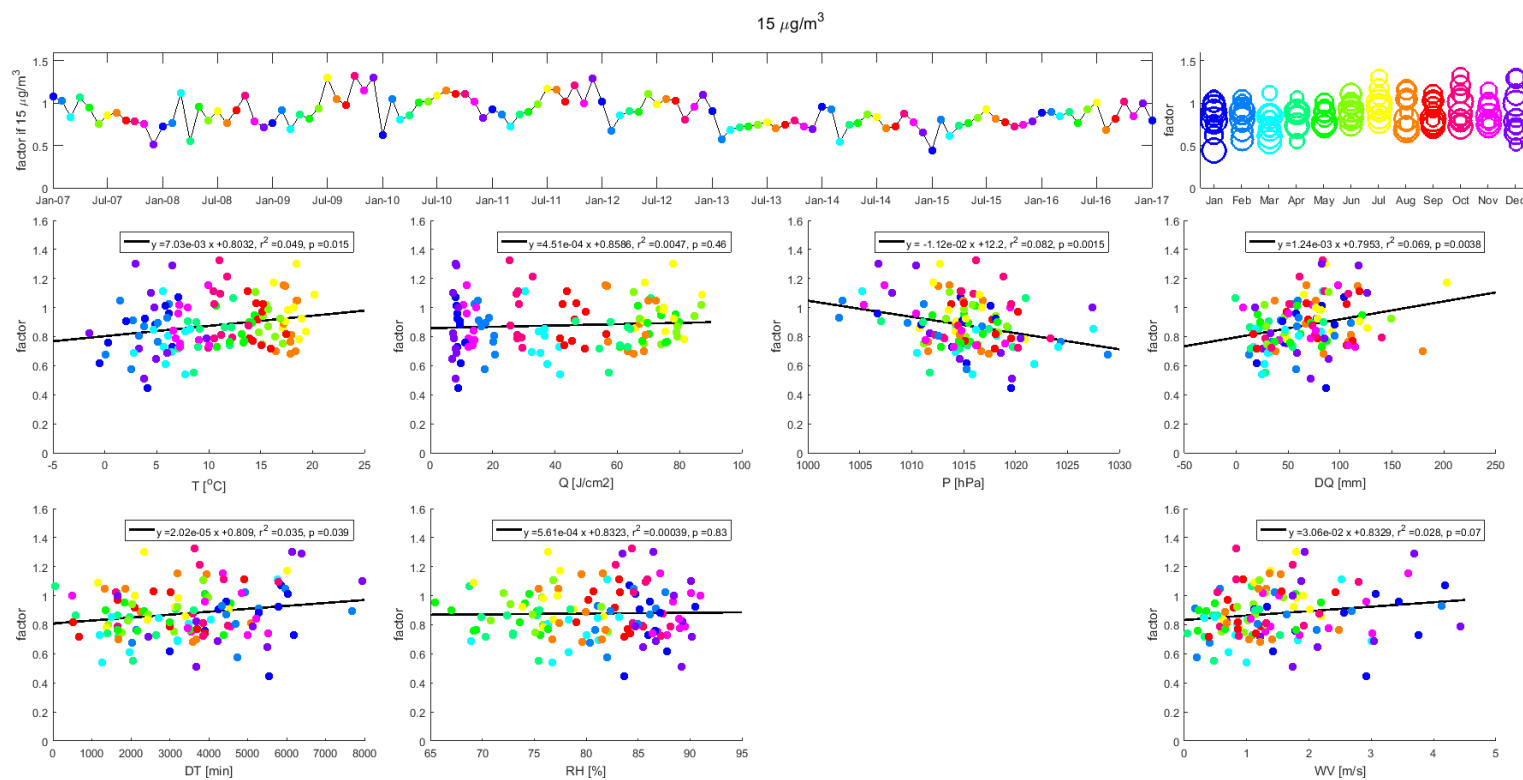


Figure B11.4 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 for a concentration level of about $15 \mu\text{g}/\text{m}^3$.

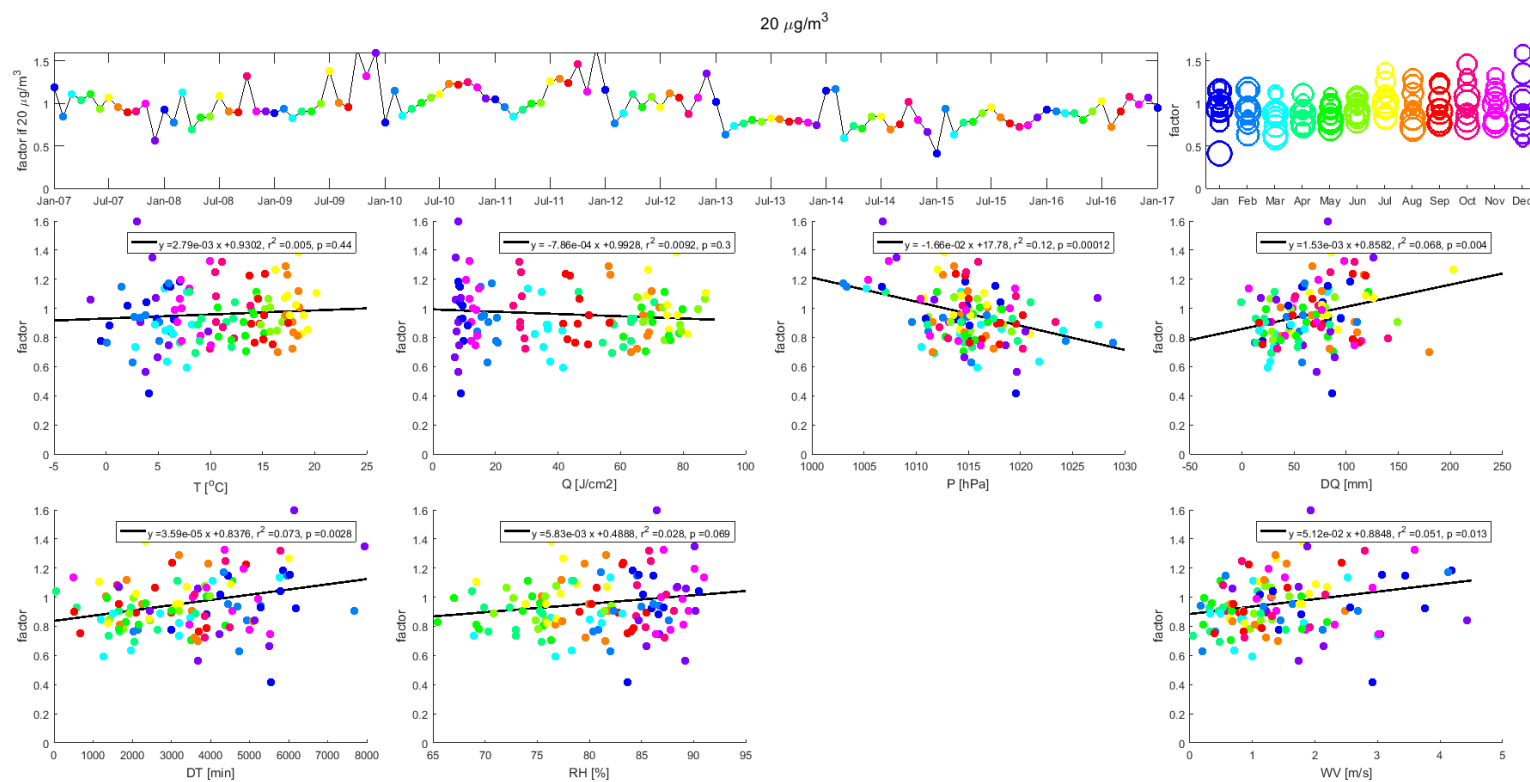


Figure B11.5 The ratio in concentration between the LML-instrument and the GRADKO tubes for the period January 2007 to January 2017 for a concentration level of about $20 \mu\text{g}/\text{m}^3$.

Appendix 12: The annual cycle in the calibration parameters

Lolkema *et al.* 2015 tested whether an annual cycle could be seen by applying a Fourier analysis. Their data were not yet corrected for the DAC (see Appendix 9) and this analysis included the first years; 2005 and 2006. In this report, the focus is on the years after 2006; data for the years 2013 through 2016 have now become available. Therefore the analysis is repeated here.

Figure B12.1 shows the variations in the original version of Lolkema *et al.* (yellow), the non DAC corrected values for the period after 2007 up to and including 2012 (purple), the period from 2007 up to and including 2012 DAC corrected (red), and the entire data set DAC corrected (blue).

For parameter *a*, there is clearly a peak in the offset at 1 year, which means that there is an annual cycle present. The DAC correction decreases the size of the peak slightly. Adding the recent years (blue line) gives a peak at 1 year that is exactly the same, but the height of the periods (or frequencies) just before and just after are also higher, making the peak less explicit.

For parameter *b*, a peak is also present after disregarding the first two years (compare yellow to purple). The DAC conversion has hardly any influence.

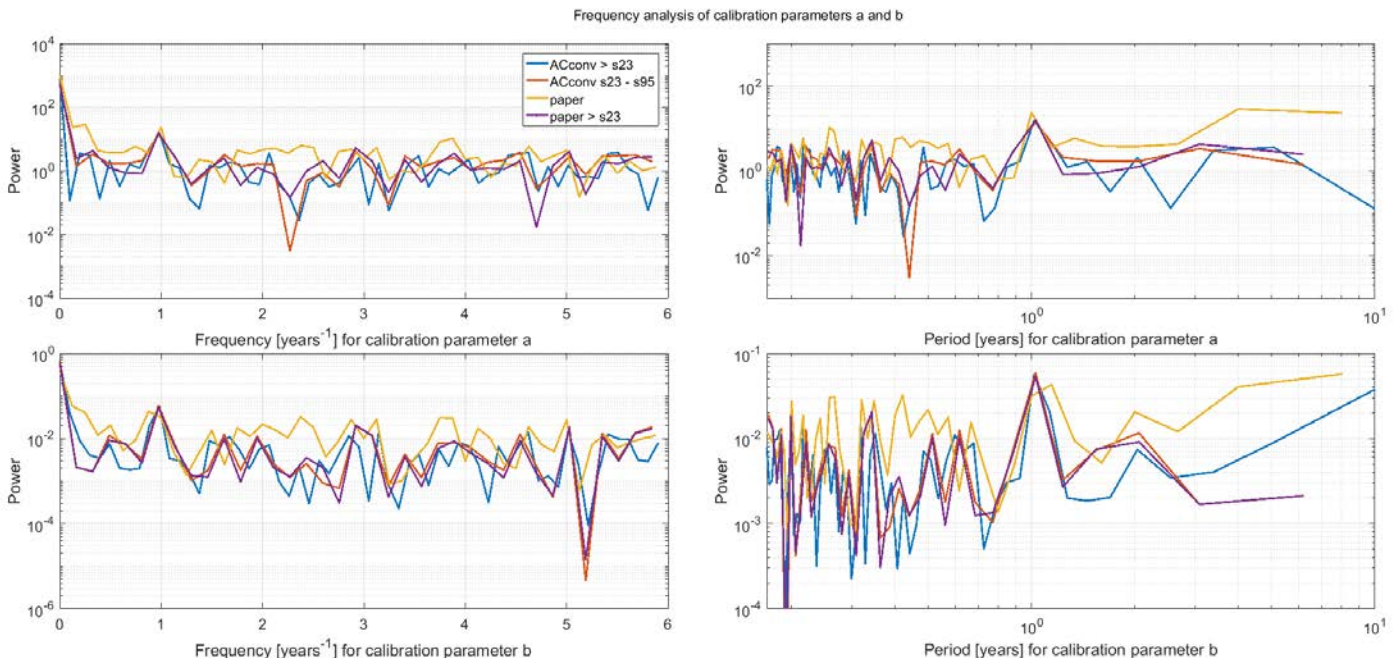


Figure B12.1 Frequency analysis of calibration parameters *a* (offset) and *b* (slope), as in Lolkema *et al.* 2015. The different colours indicate different data sets: the entire data from 2007 corrected for DAC (blue), the dataset corrected from 2007 to 2012 (red) and uncorrected (purple) and the dataset including the first two years up to and including 2012 (yellow).

Meteorological sensitivity

In Figures 14 and 15 (Chapter 3), it can be seen that a and b both have a cycle through the year, where a has a maximum during summer months (i.e. the correction in the summer months is smaller than in the winter months) and b during the winter months. It is therefore to be expected that the correlation of T and Q with a is positive, and negative with b , while the correlation of RH with a is negative and with b positive. The model shows that for a , the temperature and relative humidity are the most important parameters while for b , radiation and pressure are the most important parameters.

Table B4 The calibration constants relative to meteorological parameters

1	Calibration constant		r^2
a	Offset	$= 1.18 + 0.16 \frac{T}{T} - 0.71 \frac{RH}{RH}$	0.16
b	slope	$= 0.97 - 0.0098 \frac{Q}{Q} - 0.95 \frac{P}{P}$	0.17

Appendix 13: The accuracy of the standard deviations in triplicate annual averages per nature area

The estimation of standard deviations per nature reserve in section 4.1, based on annual averages over the period 2012-2014, is not very accurate due to the limited number of measurements. A triplicate measurement yields three annual averages annually, with which the dataset contains only nine measured values per nature reserve. Therefore, at the six LML locations, a comparison was made of the standard deviation between three years of measurement (9 measured values) and ten years of measurement (30 measured values). At the individual locations, this gives differences between the standard deviations of both series from -20% to almost + 50%. On average, over the six LML locations, the difference between the series with 9 measured values and that with 30 measured values is only 7% (Figure B13.1).

The dataset with 9 measured values therefore offers insufficient accuracy to compare individual sample changers with each other in section 4.1. However, the comparison there between, for example, the LML exchangers as a group and the voluntary employees in the MAN, is sufficiently reliable.

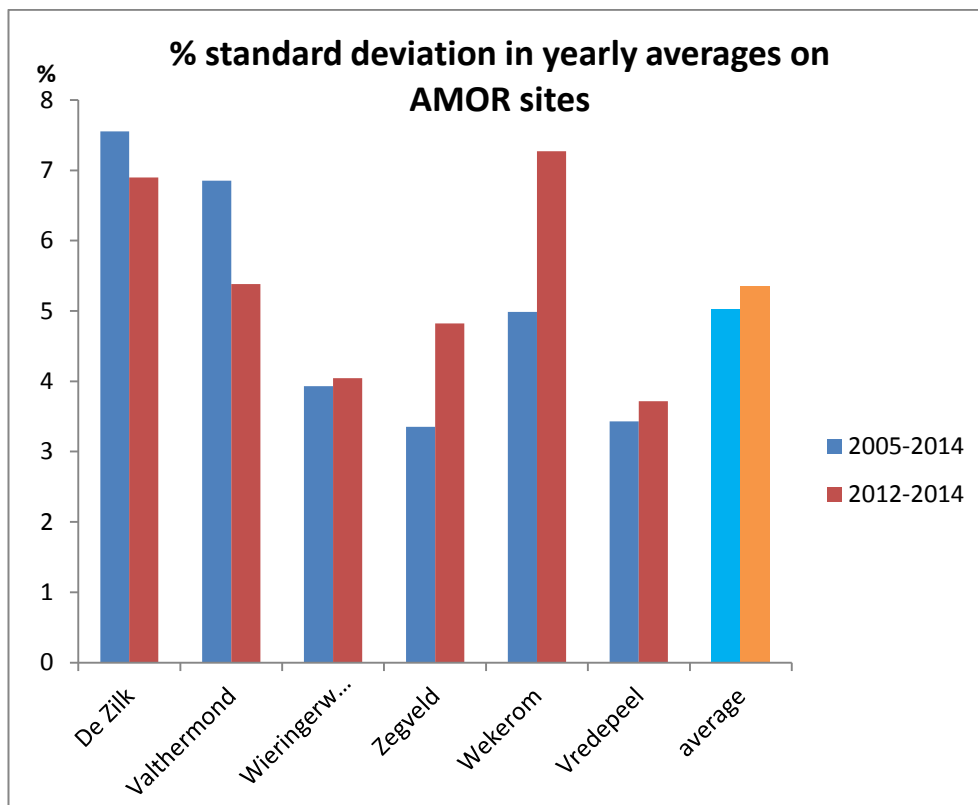


Figure B13.1: Comparison of the standard deviation in the triplicate values at LML locations, averaged over the period 2005-2014 with the same for the period 2012-2014.

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